SYNTHESIS CHARACTERIZATION AND BIOCIDAL ACTIVITY OF NOVEL HETEROBIMETALLIC CHELATES

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CHEMISTRY

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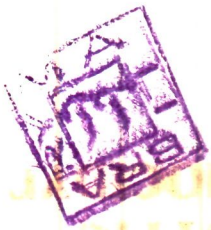

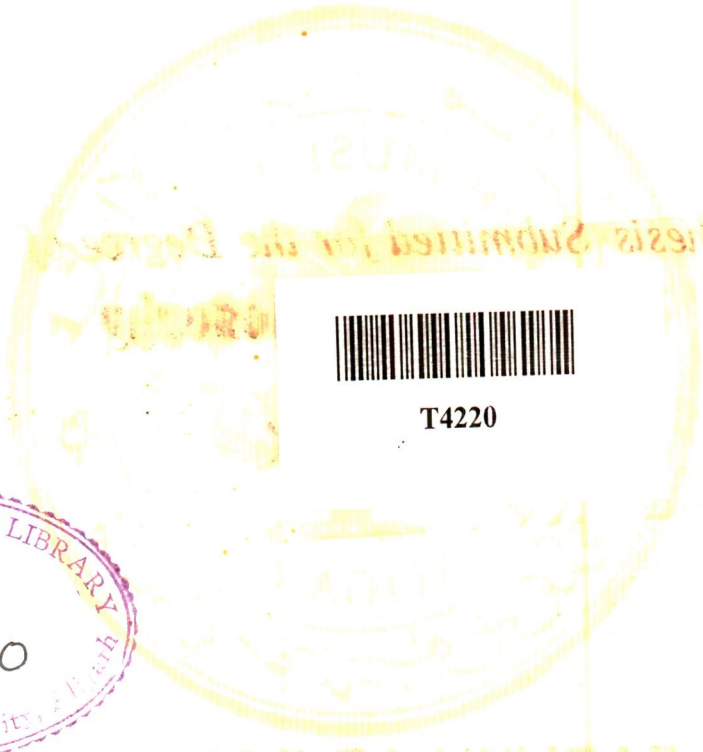

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CERTIFICATE

The work embodied in this thesis is the result of the original researches carried out by ***Farukh Arjmand*** *in this Department.*

(*K.S. SIDDIQI*)

CONTENTS

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Farukh Arjmand.

(FARUKH ARJMAND)

PUBLICATIONS

1. Heterobimetallic Chelates with 2-amino-3-formyl chromone.

   Farukh Arjmand, S. Tabassum, S.A.A. Zaidi and K.S. Siddiqi.

   Main Group Metal Chemistry.Accepted (1993).

2. Schiff base complexes as Ligand :Bimetallic Chelates of $M(SB)Cl_2$ with group(IV) metal tetrachlorides.

   K.S.Siddiqi, **Farukh Arjmand,** S.Tabassum, S.A.A.Zaidi.

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3. Novel Heterobimetallic Chelates: Condensation of (3-acetoacetyl-7 methyl-pyrano-(4,3-b)-pyran-2,5-dione) with bis 1,3-diamino propane Cu(II) chloride and Group(IV) metal tetra chlorides.

   K.S. Siddiqi, **Farukh Arjmand,** Mujeeb-ur Rehman, S. Tabassum and S.A.A. Zaidi.

   J. Chem. Res. Accepted (1993).

4. N_2S_2 Macrocyclic ligands. Synthesis and characterization of novel transition metal complexes of the type $(LM(Si_2Me_6NH)_2]^{2+}$ and $[L'M(Si_2Me_6NH)_2]^{2+}$

   K.S. Siddiqi, **Farukh Arjmand,** S. Tabassum and S.A.A. Zaidi.

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5. Heterobimetallic Complexes of Novel N_2S_2 Macrocyclic ligands with Group IV tetrachlorides and bis

(trimethylsilyl)amine.

Farukh Arjmand, S. Tabassum, S.A.A. Zaidi and K.S. Siddiqi.

Main Group Metal Chemistry. Communicated (1993).

ABSTRACT

Bioinorganic Chemistry is one of the major thrust area in Inorganic Chemistry where the *in vitro* chemical reactions may simulate the *in vivo* reaction. This emerging field gained momentum with the discovery of cis-platin. A variety of transition and non-transition elements are found in biological system, for instance, iron is an essential part of hemoglobin. Similarly copper is present in copper proteins like hemocyanin. It is an established fact that without these metal ions the activity of the organic portions with which they complex is completely vanished. It emphasises the importance of the metal ions in the living systems and suggests that the organic groups act simply as chelating agents. In this work the synthesis of a variety of heterobimetallic chelates under different reaction conditions has been undertaken. The structural framework for bimetallic chelates is quite distinctive and provides unique reactivity patterns, not always available to the conventional binucleating ligands.

The magnetic and spectrochemical behaviour of heterobimetallic chelates is entirely different from those containing only one metal atom or two similar atoms. In order to provide different environments in the bimetallic chelates for the metal ion sites, one transition and one non-

transition metal atom have been chosen for the purpose. Transition metal ions have inherent tendency to expand their coordination number in presence of strong donor ligands. This is true of Group(IV) metal tetrachlorides also. They form coordination compounds readily with donor ligands usually in a 1:1 stoichiometry.

An attempt has been made to synthesise heterobimetallic chelates of biologically important ligands. Heterobimetallic complexes of Group(IV) metal chlorides with bis(1,3-diaminopropane) Zn(II) chloride of the type $[Zn(dap)_2M'_2Cl_4]$ where M'=Si(IV), Ge(IV), Sn(IV), Ti(IV), Zr(IV) and R_2SnCl_2, dap = 1,3 diamino propane have been synthesised and characterized on the basis of elemental analysis, IR-UV/visible spectroscopy, magnetic moment and conductance measurements.

Heterobimetallic complexes of the type $[M(scz)_2M'Cl_4]$ were synthesised by the reaction of $[M(scz)_2]Cl_2$ with $M'Cl_4$ where M=Cu(II), Zn(II), M'=Si(IV), Ge(IV), Ge(IV), Sn(IV), Ti(IV) and Zr(IV), scz = semicarbazide. They were characterized on the basis of elemental analysis, IR, UV-visible spectroscopy and conductance measurement. It was inferred from conductance data that the $[Zn(dap)_2]Cl_2$ and $[M(scz)_2]Cl_2$ were ionic in ethanolic solution while their

bimetallic complexes were found to behave as non electrolyte in DMSO.

Interaction of 2,2-disubstituted aminopyridyl thiazolidin-4-one (apt-H) with Cu(II) or Zn(II) chlorides yielded complexes of the type $[M(apt\text{-}H)_2]Cl_2$. Subsequently, their heterobimetallic chelates of the type $[M(apt)_2M'Cl_2]$ with Si(IV), Ge(IV), Sn(IV) Ti(IV), Zr(IV) chlorides and dimethyl tin dichloride were synthesised. The probable structure of the bimetallic complexes has been proposed on the basis of magnetic moment and spectroscopic evidences. These studies indicated that the metal ions are four coordinated and ionic in DMSO. In addition, the toxicity of the chelating agents and their metal chelates has also been investigated. The metallation of the ligand was found to pronounce the toxicity which is reflected from LD_{50} values. They also act as growth inhibitor in the case of common fungi.

Complexes of 2 amino-3-formyl chromone (afc) with Cu(II) and Ni(II) metal chlorides were further metallated with Group(IV) metal tetrachlorides to get heterobimetallic chelates of the type $[(afc)_2MM'Cl_2]Cl_2$ where M=Cu(II), Ni(II) and M'=Si(IV), Ge(IV) and Sn(IV). On the basis of spectral and magnetic moment data Cu(II) and Ni(II) ions have been proposed to have a square planar geometry coordinating

through aldehydic oxygen and amino nitrogen. Group(IV) metal also appear to be four coordinated.

Complexes of Cu(II) and Ni(II) with Schiff base derived from the condensation of 2-amino-3-formyl chromone and 1,3-diaminopropane have been synthesised. These Schiff base complexes were further metallated with Group(IV) metal tetrachlorides yielding heterobimetallic chelates of the type $[M(SB)M'Cl_2]Cl_2$. The complexes are ionic in nature and the g values of the EPR spectrum of copper(II) complex indicated that it has a distorted square planar geometry.

Novel ß-diketonate (3-acetoacetyl-7-methyl-pyrano-(4,3-b) pyran-2,5-dione) has been synthesised and characterized by ^{1}H NMR, ^{13}C NMR, UV and mass spectral data. The ß-diketonate ligand was condensed with bis(1,3-diaminopropane)Cu(II) chloride in presence of Group(IV) metal tetrachlorides yielding new heterobimetallic chelates. It has been inferred from the spectral data of the chelates that both the metal centres acquire stable four coordinate geometry. Conductance measurements in DMSO show that they are ionic in nature.

Another ligand 1-nitro 2,2- bis(methyl thioethylene) was allowed to react with bis(1,3-diaminopropane)Cu(II) chloride in presence of Group(IV) tetrachlorides to yield heterobimetallic chelates. On the basis of spectral data

copper(II) has been proposed to have a square planar geometry coordinating through four amino nitrogen. Group(IV) metal also appear to be four coordinated.

Novel N_2S_2 macrocyclic ligands [SS'-diethyl (1,3-diaminopropane) dithiocarbamate] L_1 and [SS'-cyclohexyl spiro (1,3-diaminopropane) dithiocarbamate] L_2 and their complexes with Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) have been synthesised and characterized. The divalent transition metal complexes appear to be square planar and achieve octahedral geometry when treated with bis(trimethylsilyl) amine to yield new heterobimetallic complexes. In order to observe the change from transition metal to non-transition metal ion, Group(IV) tetrachlorides were chosen to react with the above macrocyclic ligands [SS'-diethyl(1,3-diaminopropane) dithiocarbamate] and [SS'- cyclohexyl spiro (1,3-diamino-propane)dithiocarbamate] to form metallated macrocycles. They were subsequently treated with bis(trimethylsilyl)amine to afford heterobimetallic chelates of the type $[LM(Si_2Me_6N)_2]$. It was observed from the conductance studies that the complexes were non electrolyte in DMSO. An octahedral geometry has therefore been proposed for these complexes.

No work on the chelating ability of the polydentate imidazole ligand with two different metal ions in different

environments has been done so far. Bimetallic chelates of N,N-tetrakis(2-benzimidazolyl)methyl-1,2-ethanediamine(TBED), SS'-bis(thiomethyl benzimidazole) (TBM) with Co(II), Ni(II), Cu(II) and Zn(II) nitrates and Si(IV), Ge(IV), Sn(IV), Ti(IV) and Zr(IV) tetrachlorides and diethyltindichlorides have been synthesised to yield the complexes of the type, $[M(TBED*)MCl_2](NO_3)_2$ or $[M(L*)_2M'Cl_2](NO_3)_2$ where L= TBM and BTMB. They were characterized on the basis of elemental analysis, IR, far IR, UV/visible, EPR spectroscopy and magnetic moment data. The conductivity measurements indicated that they are ionic in DMF and DMSO, The transition metal ion is octahedrally coordinated whilst the Group(IV) metal atoms have a tetrahedral geometry.

INTRODUCTION

The chemistry of multicomponent system has developed so tremendously that it has become easy to synthesise bi,tri- or polynuclear complexes .

Recently Gianfranco et al[1] have synthesised decanuclear, homo -and heterometallic polypyridine complexes and studied the physico-chemical properties related to electrochemical oxidation, intercomponent energy transfer etc.[2] The choice of Ru(II) and Os(II) polypyridine complexes was ideal to synthesise luminescent and redox-active oligonuclear species where energy and electron transfer can be driven by light. Such a procedure is based on the use of complexes in the place of both the metal (M) and the ligands (L) in the synthetic reaction, $M + nL \longrightarrow M(L)_n$.

Application of metal complexes as biocide and as medicine has been extensively made.[3] The area of dinucleating ligands capable of forming homo -and heterodinuclear complexes is of great interest because of a variety of reasons[4-6]. First, they serve as models for metalloproteins such as superoxide dismutase, oxidases and peptidases. Second, the dinuclear copper containing complexes are biologically important as two copper centers in the active site of copper proteins like hemocyanin, transport oxygen and the monooxygenase tyrosinase and

dopammine ß-hydroxylase incorporate oxygen into organic substrates. Third, dinuclear complexes can be exploited as bifunctional catalysts as shown by Mckenzie for dipalladium complexes in the catalytic hydration of acetonitrile. They have suggested a bimetallic pathway involving concerted action by the two metals in $LPd_2(MeCONH)$ and $L^*Pd_2(MeCONH)$ where L and L^* are the binucleating ligands (Fig.1). $L^*Pd_2(CH_2CHCONH)$ catalyses specific hydration of acrylonitrile to acrylamide[7].

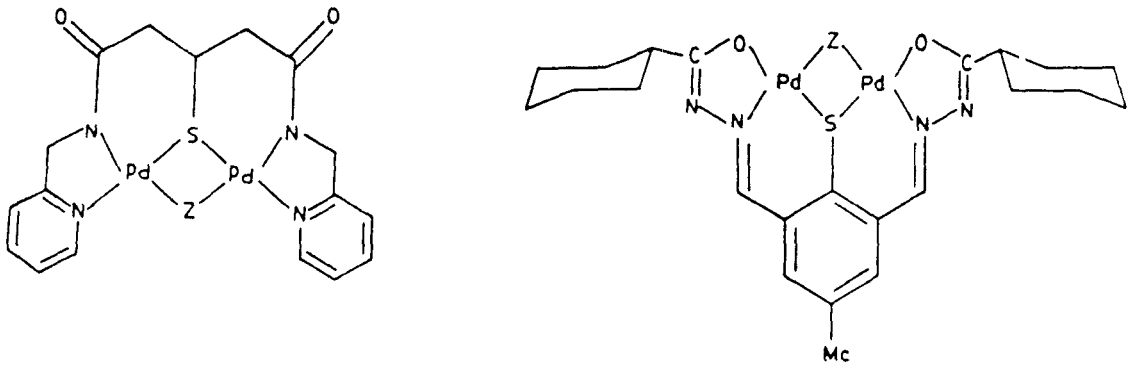


Fig. I

Carroy and Lehn[8] have reported the synthesis of dinuclear complexes of macrocyclic cryptands (homometallic or heterometallic).

The results help us to demonstrate that three basic

requirements can be met for catalysis of condensation processes at bimetallic sites.

i) The site may accommodate two potential reactants in close proximity.

ii) bond formation between the two can occur and

iii) the newly formed bridging species can be released so that cycle can be repeated.

A binucleating macrocyclic ligand which embodies 6 and 4-coordination sites has been synthesised by Fraser et al.[9] Both homobimetallic and site-specific heterobimetallic complexes of Zn(II), Co(II) and Mn(II) have been characterized (Fig. 2a, 2b). The dimanganese(II) species reacts with dioxygen to give a mixed valence compound containing both Mn(II) and Mn(III). All the manganese containing complexes are effective catalysts for the oxygenation of styrene using iodoso-benzene. The notable exception is that of dioxygen binding where the redox cooperativity of bimetallic complexes has been demonstrated.[10-12]

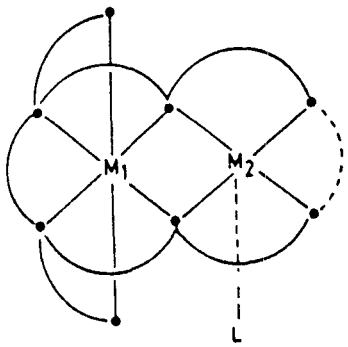


Fig.2a

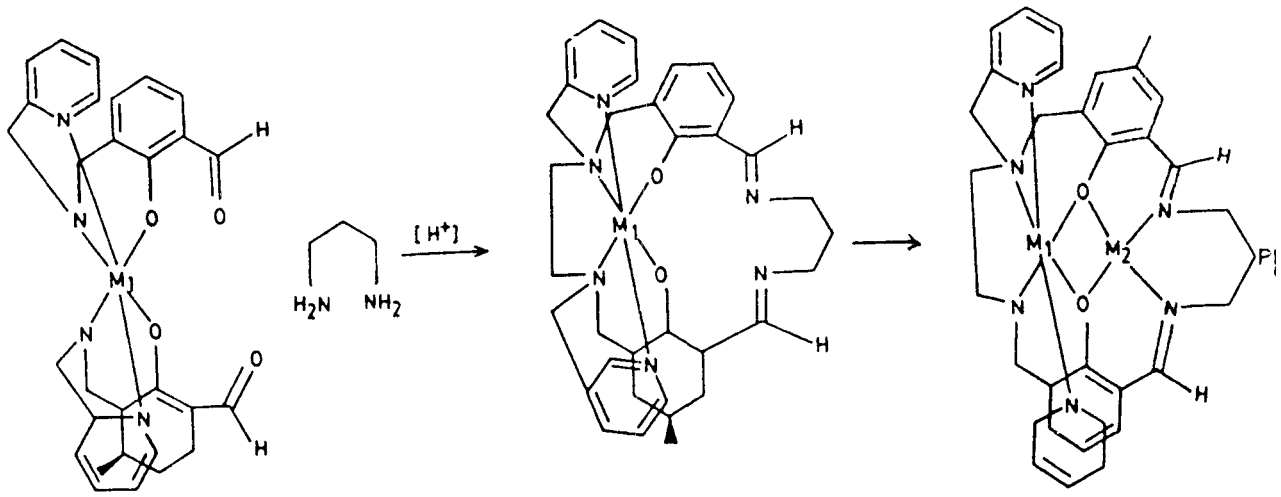


Fig.2b

Fig.2 (b) Outline of the procedure generating heterobimetallic cyclic complexes.

Macrocycles have been synthesised via two different routes namely template and nontemplate. One of the earliest examples of metal directed reactions involves the interaction of bifunctional alkylating agents with coordinated dithiolates to produce a new chelate ring with the carbon chain of alkylating agent linking two sulphur atoms in the macrocycle.[13] Another template N_2S_2 macrocycle was produced by the reaction of 2,2'-[orthophenylene bis(methylenethio)] bis(ethanamine) nickel(II) with acetone.[14-15] Reaction of multidentate dihydrazine ligand with formaldehyde and nickel(II) salts also formed the N_2S_2 macrocycles.[16] Curtis and Hay[17] reported N_2S_2 type macrocycles by nontemplate

synthesis. Several ligands have been prepared by condensation of dialdehydes with non-cyclic diamines.[18-20]

The binucleating ligands, $C_2S_2NH(CH_2)_nSCH_2CH_2(OH)_2$ where n=2 and 3 were synthesised as well as the related copper(II) and nickel(II) trinuclear species, $M_2M'\{(C_2S_2N(CH_2)_n\ SCH_2CH_2OH_2)\}_2\ X_2$ (where M=Cu, Ni, X=NO_3, ClO_4) were reported.[21-23] The magnetic and EPR properties revealed a strong antiferromagnetic interaction between the nearest neighbour, copper(II) ions with a doublet ground state while nickel(II) ion was diamagnetic and terminal Cu(II) ions were paramagnetic with essentially non-interacting S=1 state.

The compounds of the formula $[Cu_2(tmen)_2(XA)(ClO_4)_2$ [where tmen =N,N, N',N'-tetramethylethylenediamine, XA^{2-} = a derivative of the dianion of 2,5-dihydroxy-1,4-benzoquinone with two X groups in the 3,6-positions, X = H, Cl, Br, I or NO_2] have been synthesised. They exhibit an intramolecular antiferromagnetic interaction with singlet-triplet energy gaps[24] ranging from -17.4 cm^{-1} (for X=NO_2) to -25.9 cm^{-1} for X=1 (Fig. 3)

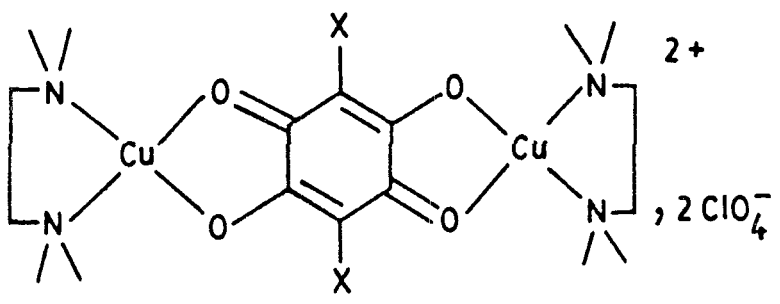


Fig.3

On the other hand, from an extensive study of a variety of metal chelates, Kahn et al[25] have shown the variation in magnetic properties of the metal ions with temperature. The compound $[Gd_2(OX)Cu(pba)_3]\ Cu(H_2O)_5].20H_2O$ where OX = oxalato and pba = 1,3 propylene bis(oxamato), was investigated for temperature dependence of zero field magnetic susceptibility and the results revealed that Gd(III) - Cu(II) interaction through oxamato bridge is ferromagnetic despite the large Gd-Cu separations (between 5.693 and 5.739A^{o}) (Fig.4).

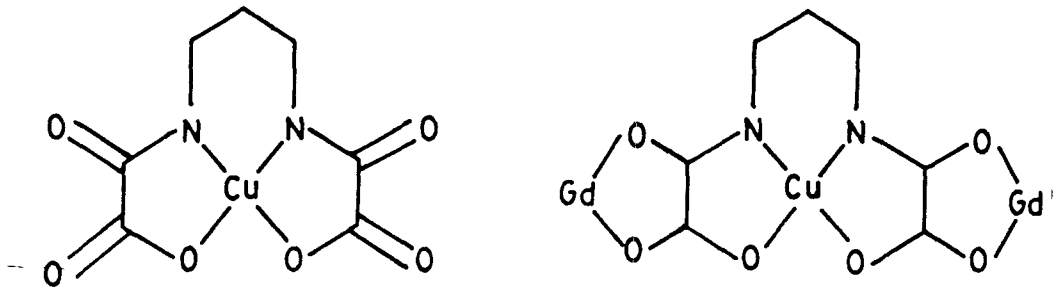


Fig.4

The ferromagnetic nature of the Gd(III)- Cu(II) interaction has been corroborated by Gatteschi et al[26-27] and Okawa et al[28], who studied Gd(III)-Cu(II) ferromagnetic interaction in di - and trinuclear species.

The condensation of primary amines with carbonyl compounds was first reported by Schiff and since then the condensation products are referred to as Schiff bases[29].

Their compounds with metal ions have been studied from different angles. Dicopper(II) complexes of unsymmetrical dinucleating Schiff base ligands bearing chemically distinct sites derived from 4-bromo-2-formyl-6-(4-methyl piperazin-1-yl-methyl) phenol and 4-bromo-2[(2-diethyl aminoethyl) ethylaminomethyl]-6-formyl phenol with 2-(aminomethyl) pyridine,2-(2-aminoethyl)pyridine, and (2-aminoethyl)-4-nitrophenol have been prepared by Crane et al[30] (Fig 5).

Such dinucleating ligands (Fig.6) have stimulated much *interest in their potential as models for dinuclear metallo-*biosites,[31-32] where the metal ions may be found in chemically or geometrically distinct environment.

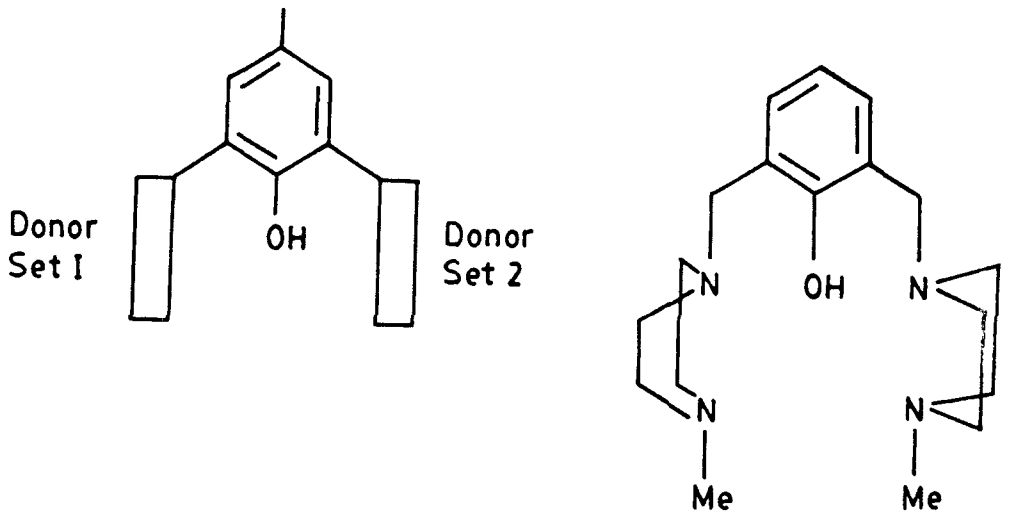


Fig.6

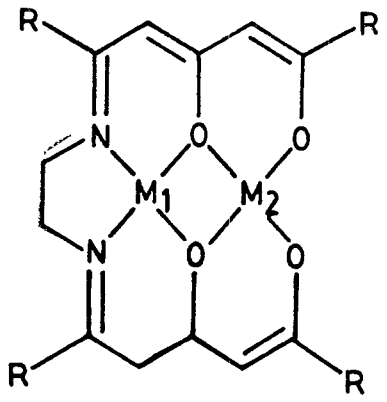


Fig.6

The nonequivalent nature of the metal coordination sites of sideoff compartmental ligands allows the preparation of hetero- and homo-dinuclear transition metal chelates.

Singh et al[33] reported the reaction of Co(II), Ni(II) and Cu(II) oximate with antimony trichloride in DMSO yielding bimetallic complexes, with the liberation of HCl. Also the reaction of cobalt(II) and nickel(II) Schiff base complexes with antimony trichloride gave bimetallic adducts in which geometrical transformation from square planar to octahedral occurred (Fig. 7).

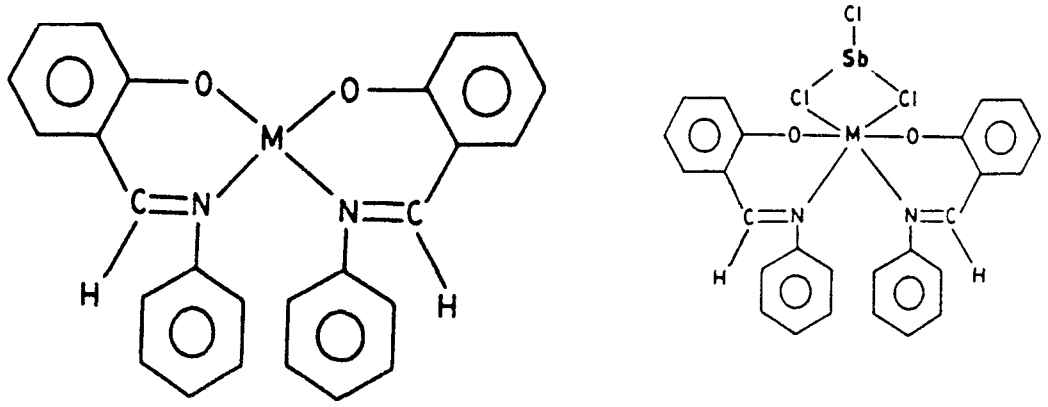


Fig.7

Complexes of transition metal ions with a large number of quadridentate N_2S_2 and N_2 O_2 ligands have been studied in view of their magnetic, electrochemical[34], and biological[35] properties. Stephan[36] developed a synthetic route for the preparation of bimetallic chelates. A complex containing an early transition metal was exploited as a ligand to be further chelated with a later transition metal yielding a bimetallic chelate.

Chromones have been used in photooxidative cyclisation of some conjugated trienes[37] . In addition, they have been shown to undergo clevage reactions[38] at position 2. The chromones react with primary amines under reflux yielding a Schiff base, its yield may be improved if condensation is carried out in a slightly acidic medium preventing the formation of an adduct with the amine. Its Schiff base provides several coordination sites and therefore, be used as a chelating agent.

Numerous copper compounds are known to exhibit antiproliferative activity.[39] Besides some prominent examples such as bleomycin and thiosemicarbazone-copper complexes[61], many other copper complexes containing Schiff base type ligands have shown antitumor activity. Neutral complex trans-bis(salicylaldoximato) copper(II)[40], and copper(II) complex salt of macrocyclic ligand (Fig.8) tetrabenzo [b, f, j, n]

1,5,9,13-tetrazacyclohexadecane[41] were found to show efficacy against experimental animal tumors.

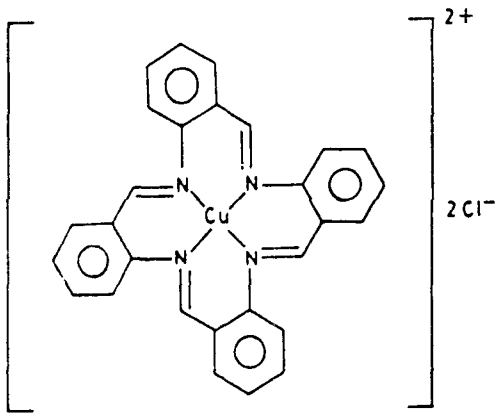


Fig. 8

Fluorescent quenching of Eu(III) by heteronuclear complexes of Cu(II) and Ni(II) of the type M Eu(fsaen)(NO_3).nH_2O [where, fsaen = N,N'-bis(3-carboxysalicylidene) ethylene diamine, n=4 when M=Cu(II), n=6 when M= Ni(II)] has been studied.[42] It was observed that fluorescent bands of Eu(III) in mononuclear EuH_2(fsaen)(NO_3).5H2O were significantly quenched on focusing heteronuclear complex as in [M Eu(fsaen)(NO_3)nH_2O] (Fig.9),

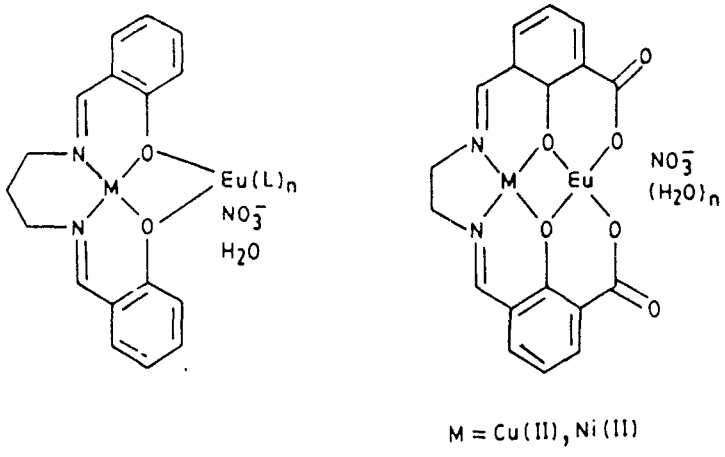


Fig.9

Heterobimetallic complexes containing(cyclopentadienyl) ethane ligands have been reported by Buzinkai and Schrock.[43] Tethering two different metals to each other via a relatively short flexible linkage (Fig.10) have helped the reactions that do not take place in systems containing analogous 'unlinked' cyclopentadienyl complexes.

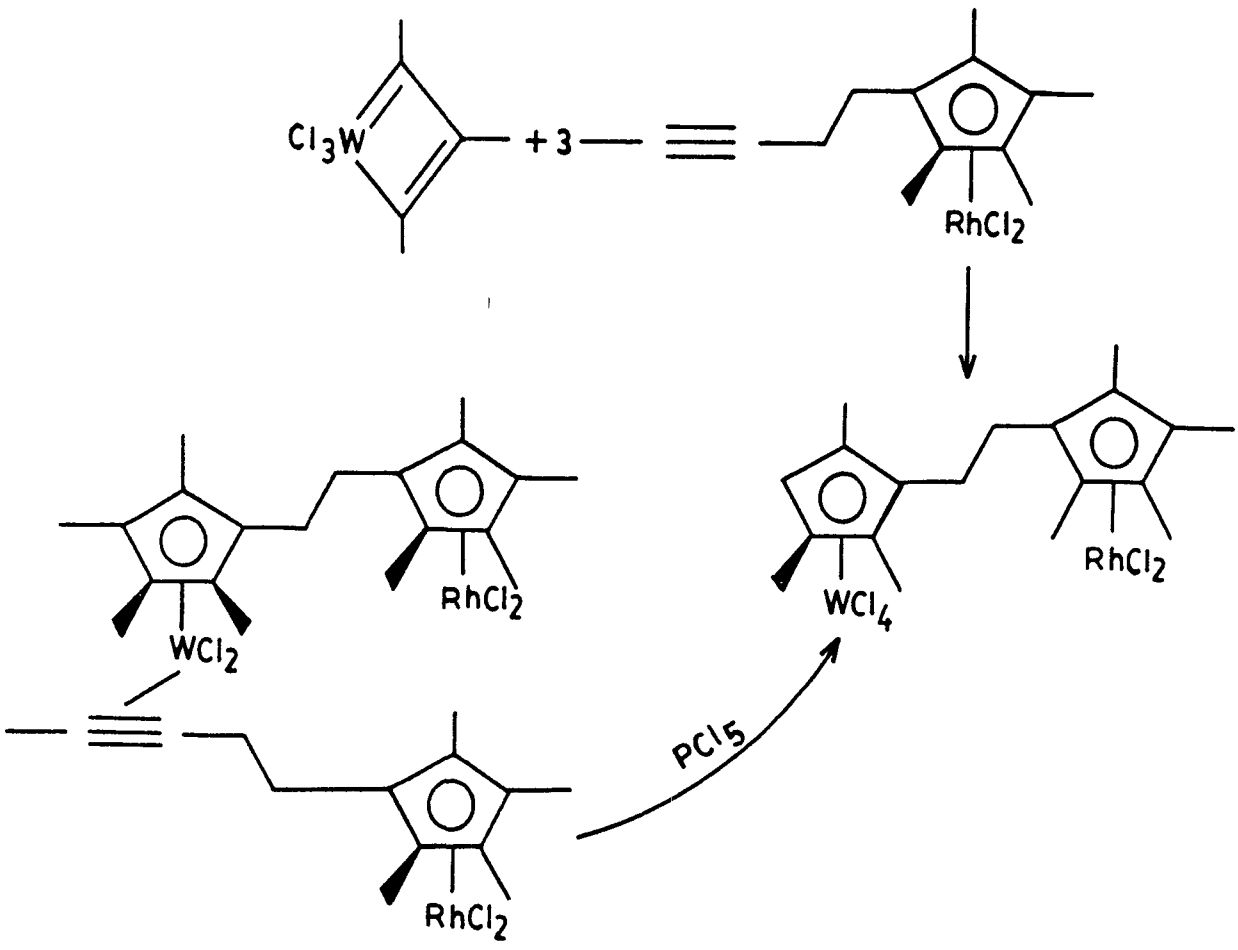


Fig.10

A large number of interesting bimetallic and polymetallic ruthenium containing systems have also been synthesised due to the building block capabilities of the the Ru(bpy) moiety(bpy=2, 2'-bipyridine)[44-51]. (Fig.11)

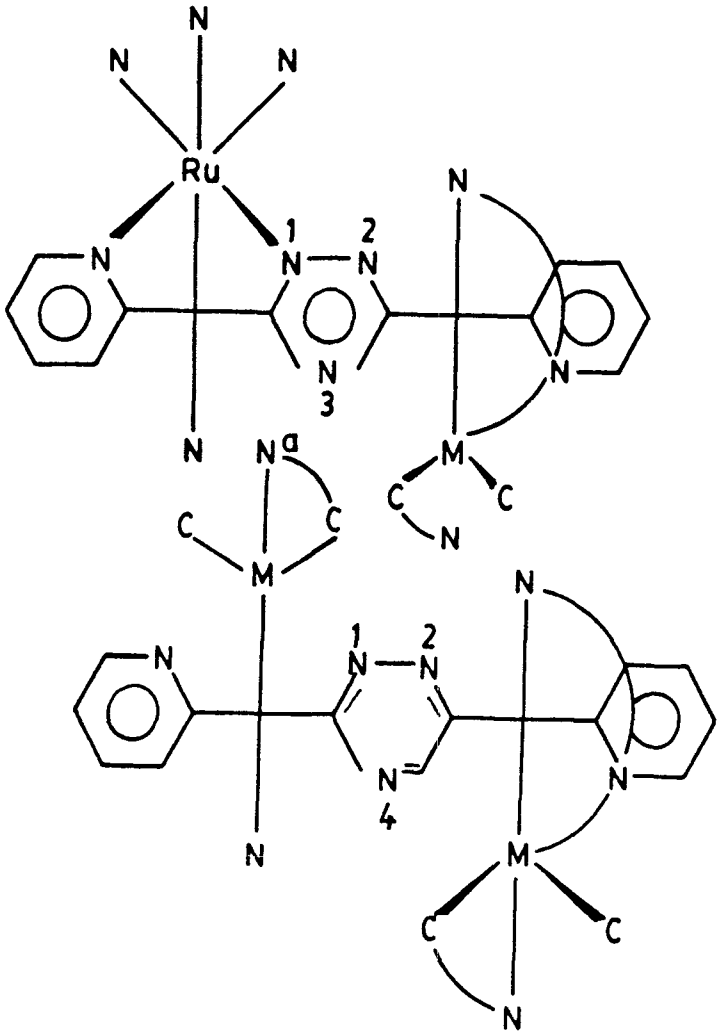
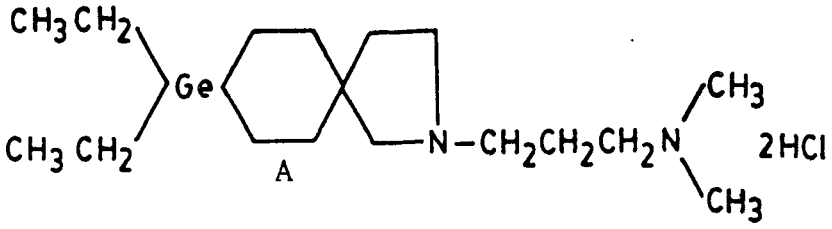


Fig.11

Not only platinum complexes exhibited antitumor properties[52] but also numerous complexes containing platinum group metals have been shown to possess cytostatic activity[53-55] Besides nonplatinum group metals main group metal compounds also exhibited anti-proliferative properties for instance, germanium and tin compounds have also been shown to act as antitumor agents. The germanium complexes may sometimes be monomeric (Fig.12 A) as in 8,8-diethyl-2[3-(N-dimethylamine propyl]-2-aza-8-germaspiro [4,5] decane or polymeric as in bis [(carboxy ethyl) germanium] trioxide[56-57] (Fig.12B).



A

$[(Ge\ CH_2CH_2COOH)_2O_3]_n$

B

Fig.12

The octahedral organotinhalide complexes (Fig.13) with mono and bidentate ligands have been reported to possess anti-proliferatic activity[58] and it is worth considering that antitumor tin complexes structurally resemble cis platin or

other cytostatic platinum metal complexes with respect to

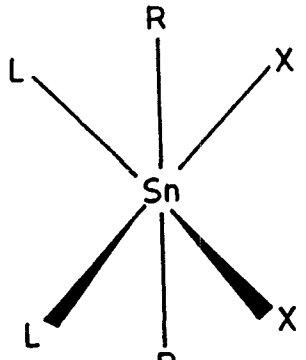


Fig. 13

the presence of cis-dihalometal moiety[59]. Investigations of organotin(IV) compounds as anticancer drug dates back[60] to 1929.Observation on structure activity relationship of the complexes has led to propose that in tin compounds the activity is related to Sn-N bond length.[61] Unlike platinum compounds, organotin compounds exhibit little toxicity at low dosage except for alkyltin compounds[62-63]. Sherman et al[64] observed that the organotin compounds containing aryl, cycloalkyl or biologically active groups are most effective antitumor agents. Development of synthetic strategies has led to a large increase in the quantity of data appertaining to heterobimetallic complexes and their characterization.They have been characterized on the basis of analytical data, spectroscopy (UV-visible, IR, NMR and EPR), magnetic susceptibility and conductance studies.[9] Recently electrochemical and photophysical properties of heterobimetallic complexes have attracted much attention but there is scarcity of literature on biological activity of these

complexes. It has been observed that biologically important ligands with metal centres have proved extremely useful in medicine. Chemotherapy is one of the important methods of treating cancer. It relies principally on the use of natural products or on purely synthetic products (some of them being the mimics of naturally occurring substances). As a consequence, much research is being done to develop synthetic metal chelates which may serve as potential antitumor drug.

PRESENT WORK

Novel heterobimetallic chelates of the type $[Zn(dap)_2M_2Cl_4]$, $[M(scz)_2M_2Cl_4]$ and $[M(apt)_2 M'Cl_2]Cl_2$ where M=Cu, Zn, M' = Si(IV), Ge(IV), Sn(IV), Ti(IV), Zr(IV) and R_2SnCl_2 , dap = 1,3-diaminopropane, scz = semicarbazide and apt = 2,2 amino-pyridyl-thiazolidin-4-one have been synthesized. The reaction has been carried out in two steps:

i. The complexes of 1,3-diaminopropane, $[Zn(dap)_2]Cl_2$ semicarbazide $[M(scz)_2]Cl_2$ and 2,2 - amino pyridyl thiazolidin-4-one $[M(apt\text{-}H)_2]Cl_2$, where M = Cu or Zn have been synthesized.

ii. The above metal complexes were treated as ligands and allowed to react with Group IV metal tetrachlorides or R_2SnCl_2 to yield new heterobimetallic chelates.

2-Amino-3-formyl chromone(afc) shows significant biological activity as an efficient bronchodilator and muscle relaxant[65-69]. Its Cu(II) and Ni(II) complexes have been synthesised and subsequently used as ligands and allowed to react with Group IV tetrachlorides to yield bimetallic chelates of the type $[M(afc)_2MCl_2]Cl_2$.

In another set of experiment complexes of Cu(II) and Ni(II) were synthesized with a Schiff base derived from the condensation of 2-amino-3-formylchromone with 1,3-diaminopropane, and allowed to react with Group IV metal tetrachlorides to give heterobimetallic chelate containing a transition metal ion and a Group(IV) atom.

Metal complexes of ß-diketonates have widely been in use as metal extractants[70-71], NMR shift reagents[72-73], in laser technology and in chemical vapour deposition[74] of copper films used in micro-electronic industry. Some of these ß-diketonato metal complexes of the type [Ti-(diketonate)$_2X_2$] are used as antitumor agents inhibiting Sarcoma 180 ascitic system[75]. In our case heterobimetallic chelates derived from the reaction of (3-acetoacetyl-7-methyl-pyrano-(4,3-b)-pyran-2,5-dione)L_1 or [1 nitro-2,2-bis(methylthio)ethylene]L_2 with bis (1,3-diamino propane) Cu(II) chloride in presence of

Group(IV) metal tetrachloride or organotin(IV) derivatives have been synthesised.

The chelates of new quadridentate N_2S_2 macrocyclic ligands, [SS' diethyl (1,3 diaminopropane)dithiocarbamate]L_1, [SS' cyclohexyl-spiro (1,3 diaminopropane)dithiocarbamate]L_2 with Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) have been synthesised and were allowed to react further with bis(trimethylsilyl)amine to achieve novel heterobimetallic chelates.

Researches on the ability of polydentate ligands containing imidazole to coordinate with two different metal ions in different coordination environments leading to the formation of heterobimetallic chelate has not been done so far. An attempt has been made to synthesise bimetallic chelates of N,N,N',N' tetrakis (2-benzimidazolyl) methyl 1-2-ethanediamine (TBED), thio-bis (methyl benzimidazole (TMB) and bis-(thiomethyl) benzimidazole (BTMB) where two different metal atoms a transition and a non transition metal ion have been introduced. In the first step, the transition metal chelates of TBED, TMB and BTMB were synthesised and treated as ligands to react with Group(IV) metal tetrachlorides to yield heterobimetallic complexes.

CHAPTER II

EXPERIMENTAL METHODS

CHAPTER II

EXPERIMENTAL METHODS

The following techniques were employed to characterise the complexes

1. Infra-red spectroscopy
2. Ultra-violet and visible (ligand-field) spectroscopy
3. Nuclear magnetic resonance spectroscopy
4. Electron paramagnetic resonance
5. Molar conductance measurements
6. Magnetic Susceptibility Measurements.

Infra-red spectroscopy

The infrared spectroscopy is a useful technique to characterize a compound. It results from transition between vibrational and rotational energy levels. IR region of the electromagnetic spectrum covers a wide range of wavelength from 200 cm^{-1} to 4000 cm^{-1}. It has been found that in IR absorption some of the vibrational frequencies are associated with specific groups of atoms and are the same irrespective of the molecule in which this group is present. These are called characteristic frequencies[76] and their constancy results from the constancy of bond force constants from molecule to molecule. The important observation that the IR spectrum of a complex molecule consists of characteristic

group frequencies makes IR spectroscopy an unique and powerful tool in structural analysis.

Ultra-violet and visible Spectroscopy

When a molecule absorbs radiation its energy is increased. This increased energy is equal to the energy of the photon expressed by the relation

$$E = h\nu$$
$$hc/\lambda$$

where h is Plank's constant, ν and λ are the frequency and wavelength of the radiation respectively and C is the velocity of light. Most of the compounds absorb light somewhere in the spectral region between 200 and 1000 nm. These transitions correspond to the excitation of electrons of the molecules from ground state to higher electronic states. In a transition metal all the five 'd' orbitals viz, dxy, dyz, dxz, dz^2 and $dx^2 - y^2$ are degenerate. However, in coordination compounds due to the presence of ligands, this degeneracy is lifted and d orbitals split into two groups t_2g (dxy, dyz and dxz) and eg (dz^2 and dx^2-y^2) in an octahedral complex and t and e in a tetrahedral complex. The set of t_2g orbitals goes below the original level of degenerate orbitals in octahedral complexes and the case is reversed in tetrahedral complexes.

Sometime due to transfer of charge from ligand to metal or metal to ligand, bands appear in the ultraviolet region of the spectrum, such spectra are known as charge transfer spectra or redox spectra.

Nuclear Magnetic Resonance

The nuclei of certain isotopes possess a mechanical spin or angular momentum. The n.m.r. spectrosocopy is concerned with nuclei having spin quantum number I = 1/2, examples of which include ^{1}H, ^{31}P and ^{19}F.

For a nucleus with I=1/2 there are two values for the nuclear spin angular momentum quantum number m = +1/2 which are degenerate in the absence of a magnetic field, In presence of magnetic field, however, this degeneracy is destroyed such that the positive value of m corresponds to the lower energy state and negative value to higher energy state separated by ΔE.

In an n.m.r. experiment, one applies strong homogenous magnetic field causing the nuclei to precess. Radiation of energy comparable to ΔE is then imposed with radio frequency transmitter is equal to precision or Larmor frequency and the two are said to be in resonance. The energy can be transferred to and from the source and the sample and

n.m.r. signal is obtained when a nucleus is excited from low energy to high energy state.

Electron spin Resonance

E.P.R. spectroscopy[77] is the branch of absorption spectroscopy in which radiation having frequency in the microwave region is absorbed by paramagnetic energy levels of electrons with unpaired spins. The magnetic energy splitting is done by applying a static magnetic field.

For an electron of spin S=1/2, the spin angular momentum quantum number will have values of ms = $\pm$ 1/2. In absence of magnetic field, the two values of ms ie. + 1/2 and - 1/2 will give rise to a doubly degenerate spin energy state. If a magnetic field is applied, this degeneracy is lifted and leads to the non-degenerate energy levels. The low energy level will have the spin magnetic moment aligned with the field and corresponds to the quantum number ms = -1/2, on the other hand, the high energy state will have the spin magnetic moment opposed to the field and corresponds to the quantum number ms = + 1/2.

Conductance measurements

The conductivity measurement is one of the simplest and easily available techniques used to study the nature of

complexes. It gives direct information regarding whether a given compound is ionic or covalent. For this purpose the measurement of molar conductance (Λ_m) which is related to the conductance value in the following manner is made,

$$\Lambda_m = \frac{\text{cell constant x conductance}}{\text{concentration of solute expressed in mole cm}^{-3}}$$

Conventionally solutions of 10^{-3}M strength are used for the conductance measurement. Molar conductance values of different types of electrolytes in a few solvents are given below; A 1:1 electrolyte may have a value of 75-95 ohm^{-1} cm^2 mol^{-1} in nitromethane, 50-75 ohm^{-1} cm^2 mol^{-1} in dimethylformamide[78-80] and 100-160 $ohm^{-1}cm^2$ mol^{-1} in methyl cyanide. Similarly a solution of 2:1 electrolyte may have a value of 150 - 180 ohm^{-1} cm^2 mol^{-1} in nitromethane, 130-170 ohm^{-1} cm^2 mol^{-1} in dimethyl formamide and 140-220 ohm^{-1} cm^2 mol^{-1} in methyl cyanide.

Magnetic Moment

When a substance is placed in an inhomogenous magnetic field it is either attracted towards the strong part of the field or repelled towards the weaker part. If it is attracted by the field, it is said to be paramagnetic, if repelled it

is said to be diamagnetic. The force F with which a diamagnetic substance is repelled when placed in a field of strength H and gradient dH/dx is determined by

$$F = VH \frac{dH}{dx}$$

Where X is called magnetic susceptibility and V is the volume of the substance. The magnetic susceptibility is a measure of the change in the magnetic moment 'μ' of the atoms caused by applied field. It is determined by the Langevin's equation.

$$\chi_z = \frac{N_o e^2}{6 mc^2} r^{-2}$$

where N_o is Avogadro's number , r is the average radius of the orbits of the electrons.

Paramagnetic susceptibility is inversely proportional to the absolute temperature

$$\chi_p = \frac{C}{T}$$

where C is the Curie constant and is characteristic of the material.

The relationship between μ eff and magnetic susceptibility is given below

$$\mu \text{ eff} = 2.34 \quad (XA/T)^{1/2}$$

where T is the absolute temperature, χA is the molar susceptibility corrected for diamagnetic effects and μ eff is the magnetic moment of the compounds in units of Bohr magnetons.

Magnetic Susceptibility measurements are mostly made with Gouy method.[81]

Gouys Method

If a uniform rod of material is suspended (Fig.14) with the lower end in a uniform magnetic field of magnitude H and the upper end in a lower field of magnitude H_o, the material will be pulled down with a force given by the expression.

$$\text{Force} = \Delta wg = 1/2 \; A \; (K-K_o) \; (H^2 - H_o^2)$$

where Δw is the apparent increase in weight of the sample upon turning on the field, g is the gravitational constant, A is the crossectional area of the material and K

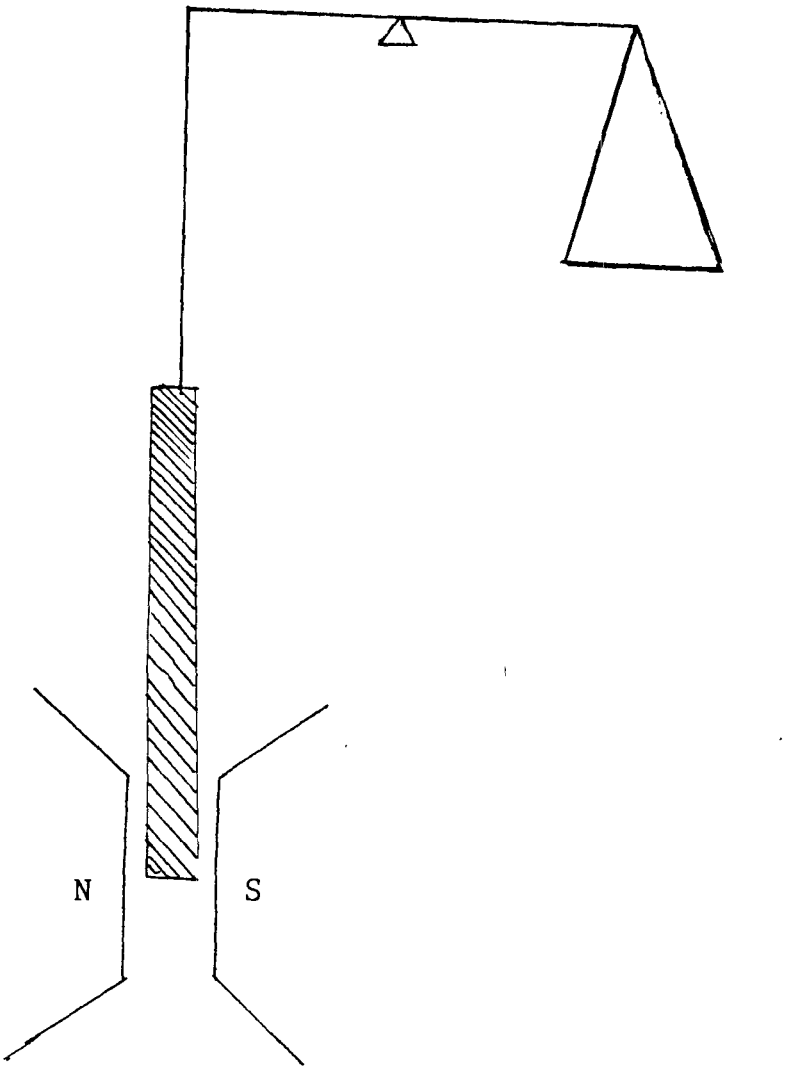


Fig.14: Schematic representation of Gouy balance

and K_o are volume succeptibilities respectively of the material and displaced medium usually air.

Usually K_o is negligible compared to K, and if the rod of material extends above the pole pieces a distance greater then eight times the pole gap width, H_o is neglibile compared to H then we write

$$K = \frac{2 \Delta wg}{H^2 A}$$

It is necessary to account for the diamagnetism of the sample tube.

$$\Delta w \text{ (corrected)} = \Delta w(\text{sample and tube}) - \Delta w \text{ (empty tube)}$$

The gouy method may be used to determine the susceptibility of either a solution or a solid. In case of a solid, the sample should be ground to a fine powder to avoid anomalies owing to an isotropy in the crystal and to facilitate uniform packing. When gram suscpetibility and molar susceptibility of a solid sample are calculated, the density used in the equation is the bulk density of the powdered material

$$\chi \text{ solution} = \frac{\chi M \text{ (solute)}}{M} \quad P - 0.720 \times 10^6 \ (1-p)$$

where M is the molecular weight of the solute and p is the solute's weight fraction.

Faraday Method

For the determination of the susceptibility of solid samples that are too small for the Gouy balance method, the Faraday method can be applied. In this method, a very small sample, (even one small crystal can suffice) is suspended from a sensitive balance in a very nonhomogenous magnetic field. The weight is determined with and without the magnetic field, and w is corrected for the diamagnetism of the sample container by use of equation

$$\Delta w \text{ (corrected)} = \Delta w \text{ (sample tube)} - \Delta w \text{ (empty tube)}$$

If K_o (the volume susceptibility of the displaced medium) is negligible, we may write

$$K = \frac{g \Delta w}{VH\ (dH/dx)}$$

where V is the volume of the sample and (dH/dx) is the magnetic field gradient.

Then for gram susceptibility

$$\chi = \frac{g \Delta w}{wH\ (dH/dx)}$$

where w is the sample weight.

Another useful method for measuring magnetic susceptibilities is the Evan's method or nmr method. The Shift of the proton resonance lines of inert reference molecules in solution is caused by the presence of dissolved paramagnetic substances. The magnetic moment of the complexes was calculated at room temperature by Evan's method[82] employing the expression

$$\mu_{eff} = 0.0618 \left(\frac{\Delta f}{f} \times \frac{T}{M} \right)^{1/2}$$

where f = oscillator frequency expressed in MHz, T = absolute temperature, M = molarity of the solution and Δf =the difference in frequency between two reference signals.

The magnetic moment for one free electron in the ligand containing cu^{2+} ion has been found to be 1.742 BM which is exactly within the prescribed range. After coordination with Group IV metal, the μ_{eff} values goes down slightly which may be ascribed to diamagnetic effect.

The reduction in the magnetic moment may also occur either due to metal interaction but solitary electron and cu^{2+} ion does not permit such interaction or it may occur through bridging group as in superexchange phenomenon. It may also be ascribed to antiferromagnetism[83].

Toxicity and probit analysis

To investigate the toxicity of the ligands and their complexes in term of LD_{50} the graphical method has been used, while the fungitoxicity was determined by agar plate method.[84]

The toxicity of a substance in terms of probit is determined against the stimuli of living organisms. Usually the stimulus is applied in a series of experimental range and the reaction of each range is determined from its application to a set of experiments.

Varying concentrations of the compound are prepared and a set of insects are exposed (or fed) to each concentration level. For each set of insects, count is made at the total number of insects(n) and number killed(r). The result can be expressed either as a proportion (r/n) or as a percentage 100(r/n). Such data may then be applied for probit analysis in assessing the various toxic substances and lethal doses.

Tolerance limit

The maximum concentration limit of a chemical at which a given set of insects survive is known as tolerance limit. For most of the biological preparations the distribution of λ is not normal but it is at least approximately normal for $X = \log_{10}$. In probit analysis, therefore, the log of the

concentration is used. It is referred to as the dose in terms of actual concentration expressed in milligram/litre and the $\log_{10}$ concentration is referred to as the dosage.[85] A plot of the percentages killed against dosage gives a sigmoid curve. The analysis of results from the sigmoid curve presents some rather serious difficulties. The percentage is transformed such that with a normal distribution of the transformed percentages would lie in a straight line. Any variation from the normal curve will cause the plotted probits to vary from a straight line. Generally, the observed variations from a straight line are of two types. In the first place the sets of experiment may not be all uniform. This will end to produce an abnormal scatters of the points about the straight line. In the second place the transformation of the dose to dosage may not be suitable.

Practical application of probit analysis

Since we expect to get a straight line when probits are plotted against dosage, the methods of linear regression are suggested.

To measure the potency of the preparation it has been found that the dose giving a 50% kill is the most statistic and referred to as LD_{50} (median lethal dose). In experiments where the response is not death we refer to the ED_{50} (median

effective dose). Whatever practical advantages there may be in knowing the LD_{90} or some similar value, the fact is that much greater precision can be obtained in the measure of the LD_{50} which is corresponding to a probit value of 5.

Another factor to be measured is the range of the dosage required for a given range of percentage kill. This might be referred to as the sensitivity of the preparation tested. Obviously, if small changes in concentrations give wide range in the percentage kill, the sensitivity is high and represented by the slope of the line. The greater the slope the narrower the range in dosage for a given range in the percentage kill. The geometry of the line would seem to give, therefore, the required measure of potency and sensitivity. Taking two points X_1 and X_2, representing the dosage, on the abscissa of the graph and finding the corresponding points Y_1 and Y_2 on the probit scale, will give the slope of the line. If b represents the slope, then

$$b = \frac{Y_2 - Y_1}{X_2 - X_1}$$

This makes it possible to set up a regression equation of the type $Y = a + bx$ where $a = Y_1 - bX_1$ or $Y_2 - bX_2$.

Preparation of potato-dextrose-agar (P.D.A.) as medium was made by the following method[84]

Peeled potatoes (200g) were boiled in 500 ml of water. Extract was mixed with 20 g agar and 20 g glucose in 500 ml of water. The volume was made upto 1000 ml in Erlenmeyer flask. The flasks were plugged with non absorbant cotton. The medium thus prepared was sterilized for 15 minutes at 15 lbs pressure in autoclave.

Isolation of fungi

The vegetables, fruits and slices showing infected areas were removed by sterile scalpel and transferred in the sterilized petridishes containing P.D.A. The fungi appearing in these petridishes were isolated in pure culture. The inoculum was raised on P.D.A. by transfering mycellia from the pure culture. The compounds were screened for their antifungal activity against A. flavus and A. niger by agar plate technique at three different concentration viz. 1%, 1.5%, 2%.... Two commercial fungicides Memege and Blitox 50 WP have also been tested under similar conditions to compare the results. The number of replications in each case was three. The % inhibition in growth of the fungi was calculated by using the following formula

$$= \frac{C - T}{C} \times 100$$

CHAPTER III

SYNTHESIS, CHARACTERIZATION AND BIOCIDAL ACTIVITY OF HETEROBIMETALLIC CHELATES

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SYNTHESIS, CHARACTERIZATION AND BIOCIDAL ACTIVITY OF HETEROBIMETALLIC CHELATES

EXPERIMENTAL

1,3-Diaminopropane , semicarbazide hydrochloride (Koch Light), $CuCl_2$, $ZnCl_2$,NaOH (BDH), $SiCl_4$, $GeCl_4$, $SnCl_4$, $TiCl_4$, $ZrCl_4$, $(CH_3)_2SnCl_2$, mercapto acetic acid, ammonium carbonate (Fluka), and nicotinamide (Sigma) were used as received. IR spectra were recorded on a Perkin Elmer 240 and Perkin Elmer 621 as KBr disc (400-4000 cm^{-1}) and as nujol mull (200-400 cm^{-1}) respectively. The EPR spectra were recorded on a Bruker ESP-300-X-band spectrometer. The UV-vis spectra were recorded on a spectronic 21 spectrophotometer. The conductivity measurements were done on Elico conductivity bridge type CM-82T. Estimation of chlorine was carried out by usual gravimetric method.

Toxicity studies:

Equal number of cockroaches were taken in five cages and acclamatised. They were allowed to feed on (a) 2-2-amino pyridyl thiazolidin-4-one (apt-H) and (b) its complexes mixed with a palatable base in different concentrations ranging from 1-5 ppm (w/w). A control set was also run simultaneously and test insects were kept under observation. The percent

mortality was recorded after 96 h. The LD_{50} was calculated in terms of probit.

To investigate the fungitoxicity two separate sets of experiments were done on A. flavus, A. niger and A. pori along with a control set. A 2-3% solution of (apt-H) and its heterobimetallic complex were sprayed on a measured area of fungus colony. The inhibition in growth of the fungus colony were compared against a control set run under the same experimental conditions.

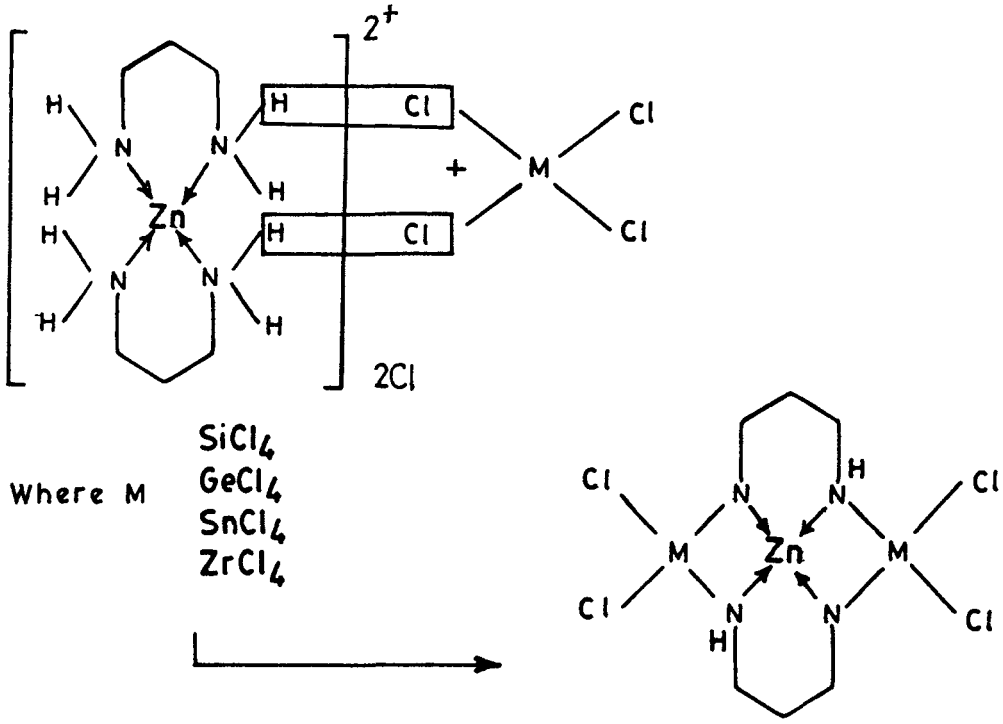
Synthesis of bis (1,3-diaminopropane) Zinc(II) chloride $[Zn(dap)_2]Cl_2$

A mixture of hydrated zinc(II) chloride (0.01 mol, 1.36g) and 1,3 diamino propane (0.02mol 1.58 mL) in 50 mL ethanol was refluxed for1h and left overnight when it yielded a precipitate.It was recrystallized from ethanol and dried in vacuo.

Synthesis of bis (semicarbazide) copper(II) chloride, $[Cu(scz)_2]Cl_2$

It was prepared by refluxing a mixture of hydrated copper(II) chloride (0.01 mol, 1.71 g) and semicarbazide hydrochloride (0.02 mol, 2.02 g) in 100 mL ethanol for 6 h. Green crystals separated out on standing the solution for 24

SCHEME I


2+
H
Cl
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+
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Cl
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H
2Cl
Where M
SiCl4
GeCl4
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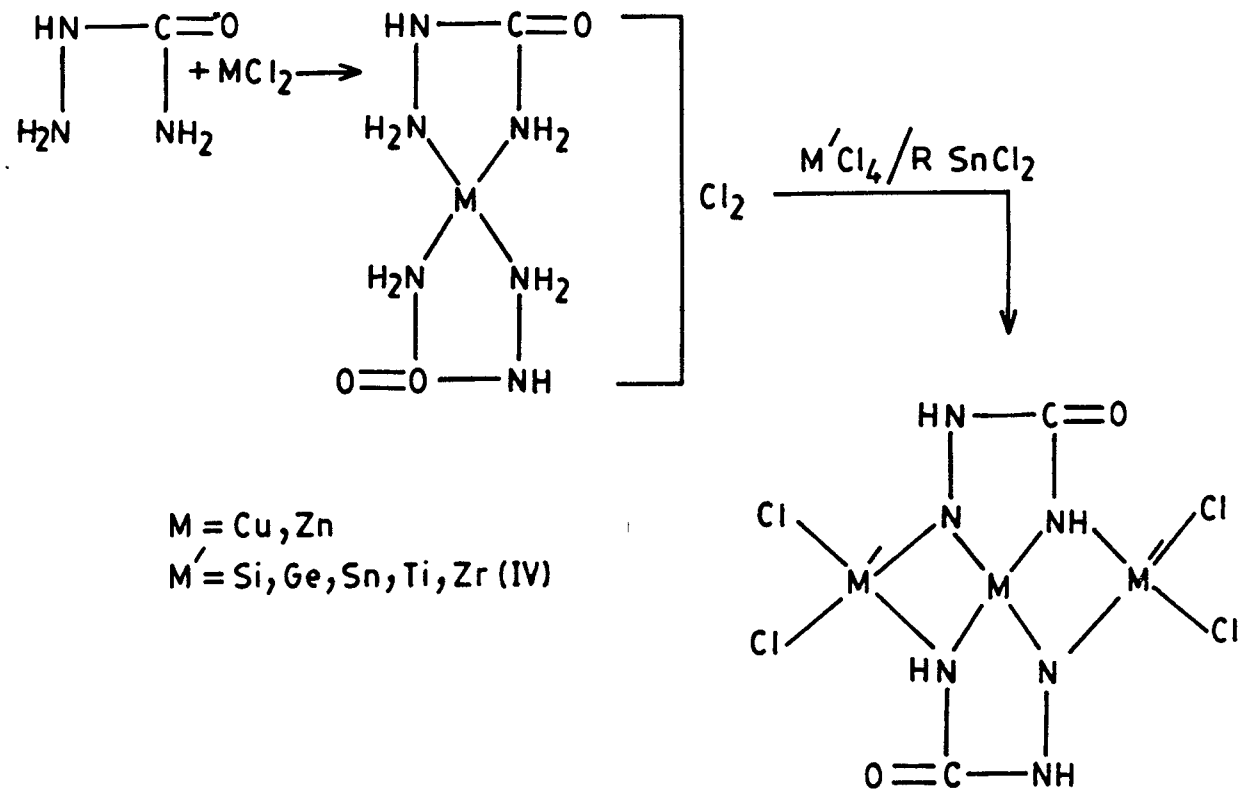
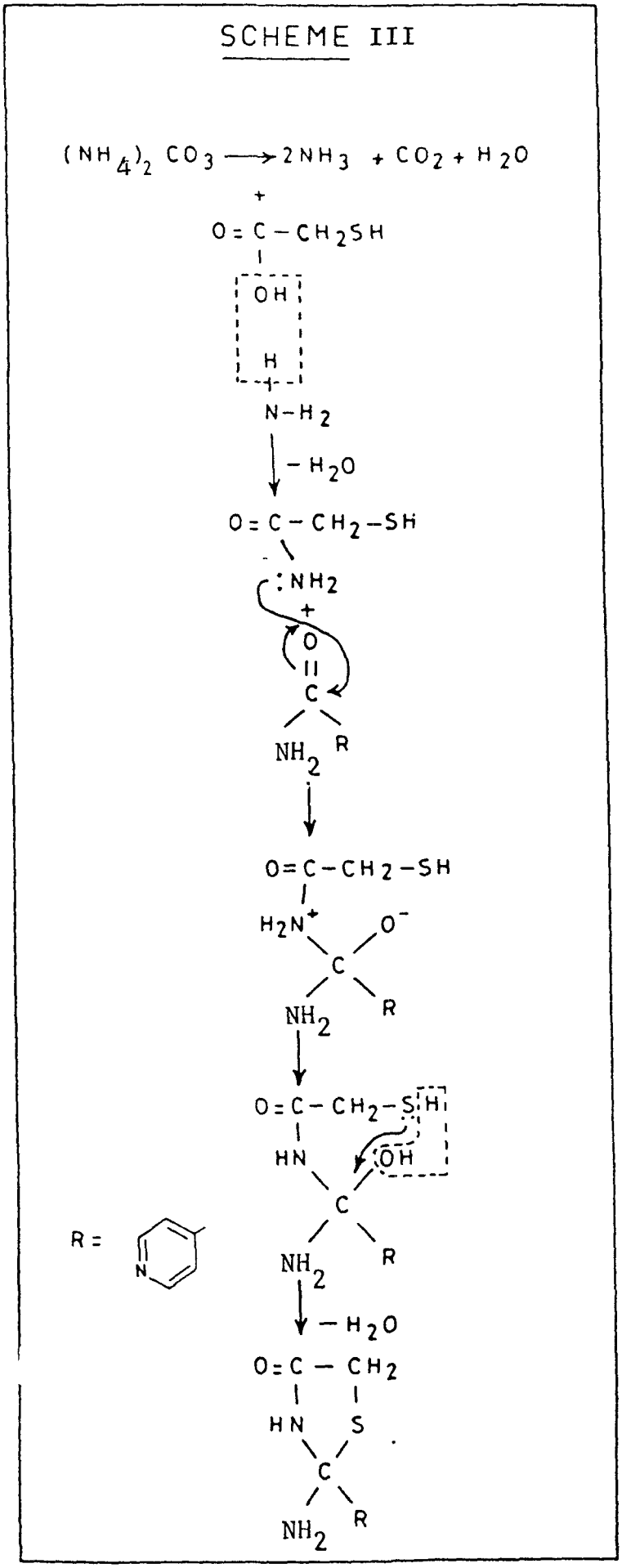
SCHEME – II



M = Cu, Zn

M′ = Si, Ge, Sn, Ti, Zr (IV)

SCHEME III


(NH4)2 CO3 → 2NH3 + CO2 + H2O
O=C-CH2SH
OH
H
N-H2
-H2O
O=C-CH2-SH
:NH2
O
C
NH2
R
O=C-CH2-SH
H2N+
O-
C
NH2
R
O=C-CH2-SH
HN
OH
C
NH2
R
R =
-H2O
O=C-CH2
HN
S
C
NH2
R

h at room temperature. $[Zn\ (scz)_2]Cl_2$ was also prepared by the same method.

Synthesis of 2,2-amino pyridyl thiazolidin-4 one (apt-H)

Nicotinamide (0.05 mol, 6.10 g), mercapto acetic acid (0.14 mol, 18.40 mL) and ammonium carbonate (0.15 mol, 11.40g) were dissolved in dry benzene (250 mL) and refluxed for 60 h. The organic layer containing benzene solution was washed thrice with water and 0.1M NaOH and finally with water. It was dried over anhydrous sodium sulphate. Benzene was removed through suction when it yield crystalline 2,2-disubstituted aminopyridyl thiazolidine-4-one (Scheme III).

Synthesis of the complexes, $[M(apt\text{-}H)_2]Cl_2$

(apt-H) (0.02 mol, 3.90 g)) dissolved in 20 mL of ethanol was mixed with hydrated copper(II) or zinc(II) chloride (0.01 mol, 1.71 g or 1.31 g) and the resulting mixture was continuously refluxed for six h and left overnight at 15^{o}C. An amorphous solid was precipitated which was filtered, washed with ethanol and dried in vacuo.

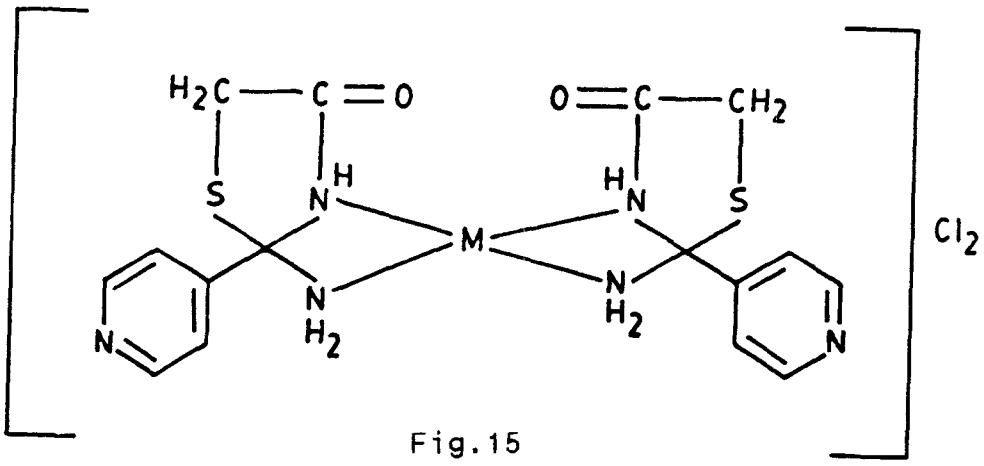


Fig.15

Synthesis of heterobimetallic complexes

Synthesis of $[Zn\ (dap)_2M_2Cl_4]$

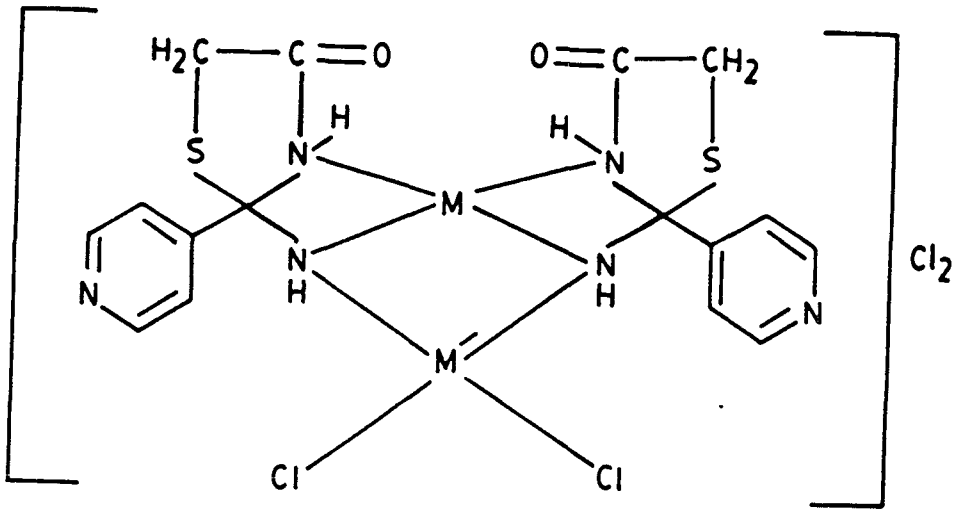
A mixture of hot ethanolic solution (20 mL) of $[Zn(dap)_2]Cl_2$ (0.01 mol, 2.84 g) and Group (IV) metal tetra chloride or dimethyltindichloride (0.02 mol) was thoroughly stirred and left overnight which afforded fine crystalline compound (Scheme I) . They were filtered and dried in vacuo.

Synthesis of $[M\ (scz)_2\ M_2\ Cl_4)$

An ethanolic soluion of $[M\ (scz)_2]Cl_2$ (0.01 mol (where M = Cu or Zn),(30 mL) in 100 mL round bottomed flask was treated with group (IV) metal chloride or R_2SnCl_2 (0.02 mol). at room temperature. Fine yellow crystals separated out when the contents were left for about 20 days at room temperature. The crystals were filtered and dried in vacuo.

Synthesis of $[M(apt)_2M'Cl_2]Cl_2$

Complex $[M(apt-H)_2]Cl_2$ (0.01 mol) (where M=Cu or Zn) dissolved in 20 mL of dimethylformamide was mixed with Group(IV) metal tetrachloride (0.01 mol) at room temperature and the resulting mixture was continuously stirred for 4h. On standing this mixture in a refrigerator overnight an amorphous solid separated out, which was washed with ethanol and dried in vacuo.



M = Cu,Zn
M′ = Si, Ge, Sn, Ti, Zr (IV)

Fig.16

RESULTS AND DISCUSSION

The analytical data of the ligands and complexes are given in Table 1. All the complexes are stable to heat and oxidation by air. They are formed by the replacement of aminohydrogen by metal which has been confirmed by quantitative assay of chlorine as AgCl. The compound $[Zn(dap)_2]Cl_2$ $[Cu(scz)_2]Cl_2$ and $[Zn(scz)_2]Cl_2$ are fairly ionic which is evidenced by their molar conductance measured in ethanol (80.50 and 84.0 ohm^{-1} cm^2 mol^{-1}) at room temperature while $[M(dap)_2M'_2Cl_4]$ and $[M(scz)_2M'_2Cl_4]$ are non-ionic in DMSO (28 ohm^{-1} cm^2 mol^{-1}). The molar conductance of $[M\ (apt)_2\ M\ Cl_2]Cl_2$ in DMSO indicated it to be ionic in nature (69-80 ohm^{-1} cm^2 mol^{-1}).

The magnetic moment of the complexes was calculated at room temperature by Evans' method[82]. The μ eff value of 1.78 BM of $[Cu(scz)_2]Cl_2$ corresponds to one unpaired electron. However, a negligible decrease in magnetic susceptibility for heterobimetallic complxes is probably due to the diamagnetic contribution.

IR Spectra

The $[Zn(dap)_2]Cl_2$ shows two N-H stretching frequencies in 3200-3500 cm^{-1} region which undergoes a substantial negative shift after chelation. However, the δN-H appearing

at 1585 cm^{-1} and 1385 cm^{-1}, are not altered except for a minor change in intensity.

The $[M(scz)_2]Cl_2$, where M = Cu or Zn show two bands in 3480 - 3450 cm^{-1} region and a sharp band at 1650 cm^{-1} have been assigned to ν NH (amide bands), and ν C=O respectively. The NH bands undergo a shift to lower wave number (ca 60-85 cm^{-1}) after complexation with Group(IV) metals. This may be due to the replacement of a proton from νNH_2. The C=O stretching frequency, however, remains unaltered indicating that its non involvement in coordination.

In the present case the thiazolidin-4-one has apparently four coordination sites. However, for steric reasons all the sites may not be prone to coordiantion. Two strong bands (3150 cm^{-1} and 3250 cm^{-1}) in free ligand due to νNH (secondary amine), νNH_2 (primary amine) have been observed which undergo a negative shift (3230 cm^{-1}) in the complexes. Since there is no shift in ν C=O on passing from free to complexed ligand it indicates non involvement of CO group in coordination. The IR spectra of $[M(apt\text{-}H)_2]Cl_2$ complexes show a broad band at 3230 cm^{-1} due to NH_2 group which is replaced by a new band at 3100 cm^{-1} after complexation with Group(IV) metals ions (Fig. 16). The Other

bands such as $\tilde{\nu}$ C=O (1710 cm^{-1}), $\tilde{\nu}$ C-S (760 cm^{-1}) and $\tilde{\nu}$ C=N (pyridyl, 1640 cm^{-1}) remain unaltered.

The two bands in the $[Zn(dap)_2]Cl_2$ at 1363 and 1440 cm^{-1} have been assigned to $\tilde{\nu}$C-N and $\tilde{\nu}$ C-C. The band at 1363 cm^{-1} is shifted to 1336 cm^{-1} after coordination with MCl_4. In the far IR spectra of all the complexes the $\tilde{\nu}$ (M-N) modes have been observed in the range 420-550 cm^{-1} (Table 2) The (M-Cl) bands are stronger but lie at lower wave numbers than the (M-N) bands.[86]

Electronic Spectra

The visible spectra show a broad band at 16977 cm^{-1} corresponding to d - d* transition[87] as expected for Cu(II) complexes with square planar geometry. This is further supported by EPR spectrum which displayed g_{II}(2.13) and $g_{\perp}$ (2.02).

Toxicity

The sulphur compounds have inherent pesticidal property and hence it seemed essential to investigate their toxicity against insects and fungi. The efficacy of thiazolidin-4-one atp-H, $[Cu(atp\text{-}H)_2]Cl_2$ and their heterobimetallic complexes $[Cu(atp)_2SnCl_2]Cl_2$ as pesticides is given in Table 3 (Fig. 17-18). On the basis of the mortality data the compounds may

be arranged in the asending order of their toxicity. atp-H < $[Cu(atp\text{-}H)_2]Cl_2$ < $[Cu(atp)_2\ SnCl_2]Cl_2$.

Thiazolidin-4-one and their complexes have been screened for their antifungal activities. It has been noted that the compounds containing two metals cause a greater increase in fungicidal properties than those containing only one (Table 3). The fungitoxicity of the ligands follow the same order as those found for insects. However, it is important to note that the toxicity of thiazolidin-4-one (atp-H) is enhanced after complexation.

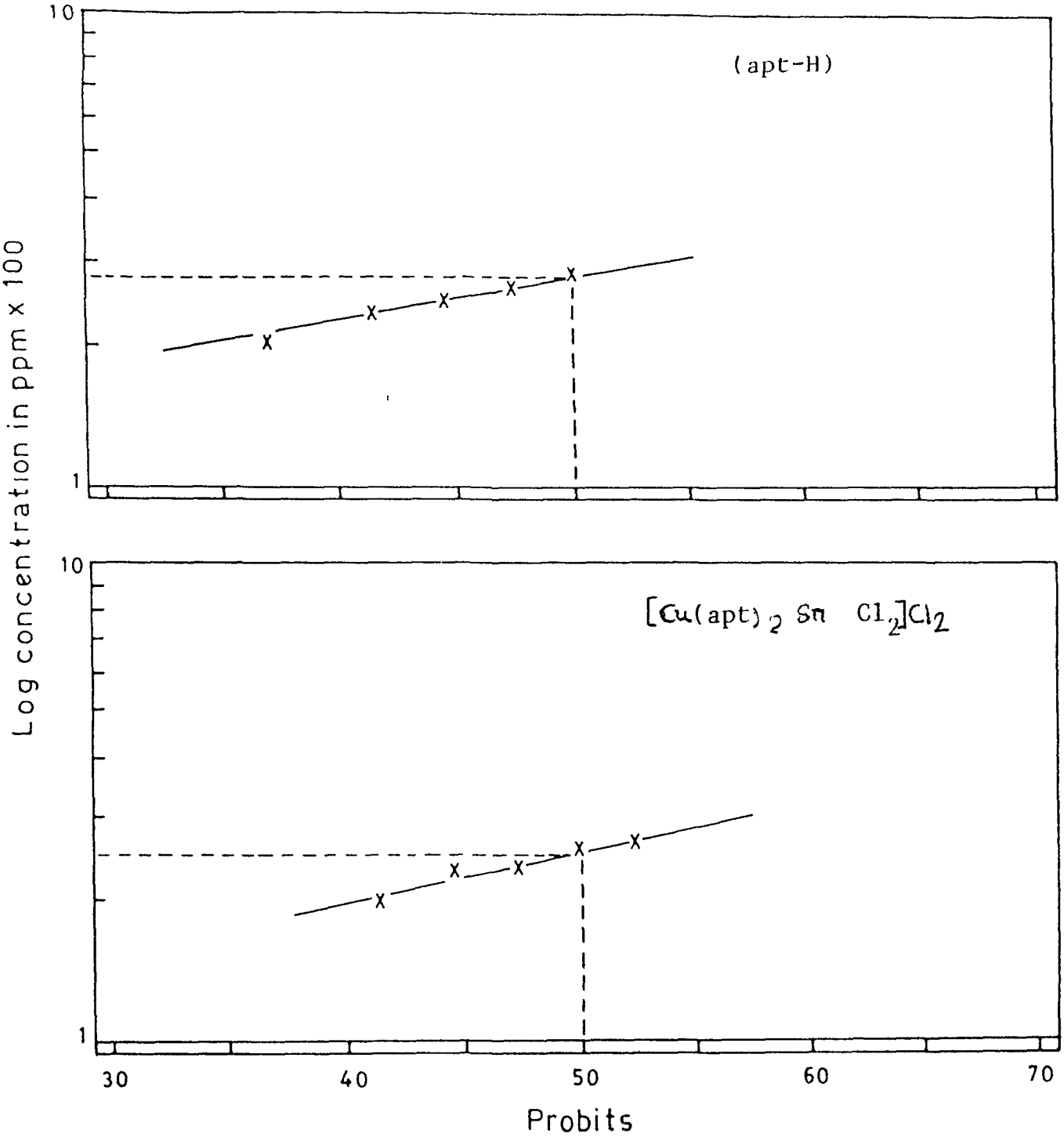


Fig. 17. Probit kill curve for Cockroach

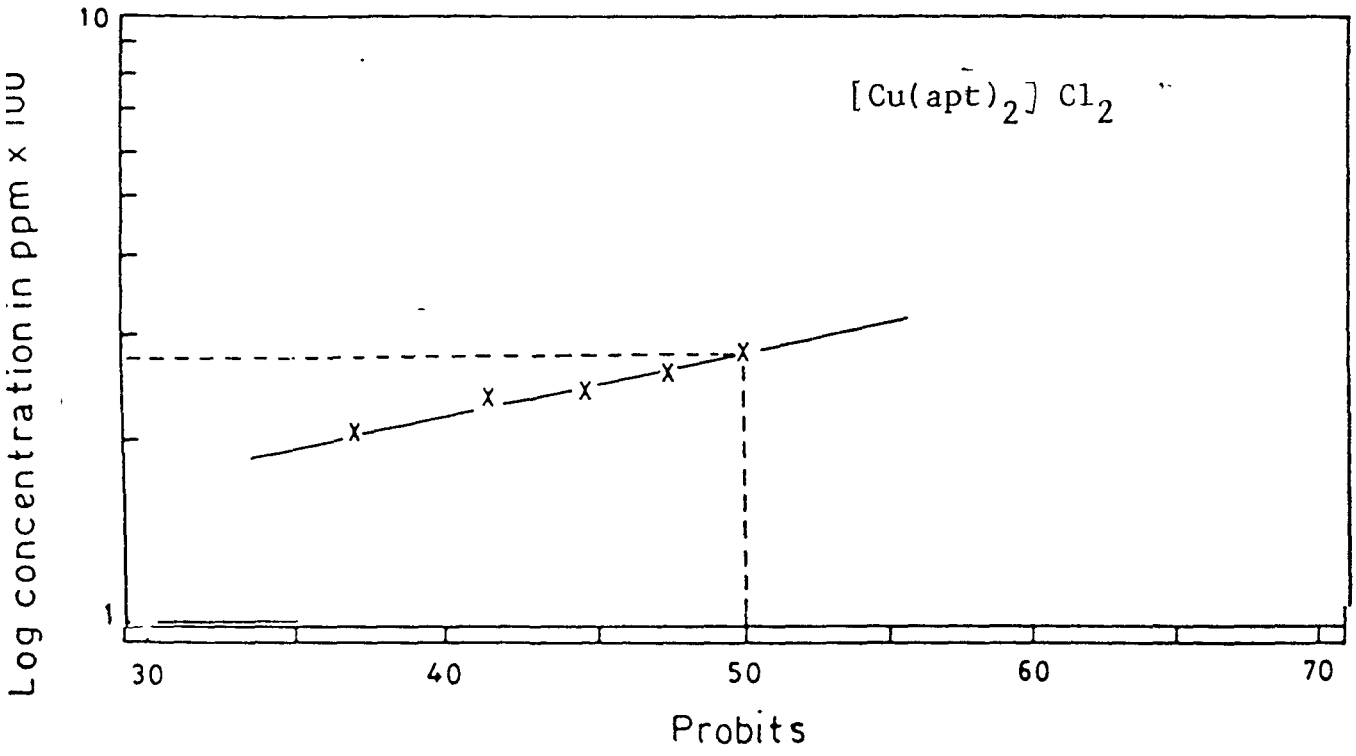


Fig.18. Probit kill curve for Cockroach

Table 1 : Analytical data, M.P., colour and yield of heterobimetallic complexes of $[Zn(dap)_2]Cl_2$, $[M(scz)_2]Cl_2$

Complexes	M.P. °C	Colour	Yield %	% Calcd. (Found)			
				C	H	N	Cl
$[C_6H_{20}N_4Zn]Cl_2$	Green	258	60	25.31 (25.51)	7.03 (7.23)	19.69 (19.77)	24.96 (25.10)
$[C_6H_{14}N_4Zn\ Si_2Cl_4]$	Yellow	263	50	17.58 (17.79)	3.41 (3.63)	13.67 (13.86)	34.68 (35.00)
$[C_6H_{14}N_4Zn\ Ge_2Cl_4]$	Orange	268	52	14.55 (14.78)	2.83 (2.99)	11.32 (11.43)	28.71 (29.13)
$[C_6H_{14}N_4Zn\ Sn_2Sl_4]$	Yellow	267	50	12.29 (12.43)	2.39 (2.43)	9.56 (9.68)	24.25 (25.06)
$[C_6H_{14}N_4Zn\ Ti_2Cl_4]$	Yellow	280	52	16.17 (16.37)	3.14 (3.29)	12.57 (12.79)	-
$[C_6H_{14}N_4\ Zn\ Zr_2\ Cl_4]$	Yellow	283	55	13.53 (13.78)	2.63 (2.78)	10.52 (10.68)	-
$[C_6H_{14}N_4Zn\ Sn_2(CH_3)_4]$	Brown	265	55	23.83 (23.98)	5.16 (5.28)	11.12 (11.33)	

Table 1 contd

Complexes	M.P. °C	Colour	Yield %	% Calcd. (Found)			
				C	H	N	Cl
$[(C_2H_{10}N_6O_2)Cu]Cl_2$	236	Green	70	8.43 (8.53)	3.51 (3.63)	29.51 (29.69)	29.95 (30.16)
$[(C_2H_4N_6O_2)CuSi_2Cl_4]$	218	Yellow	38	6.42 (6.56)	1.07 (1.18)	22.48 (22.66)	38.01 (38.93)
$[(C_2H_4N_6O_2)CuGe_2Cl_4]$	225	Orange	40	5.18 (5.29)	0.86 (1.10)	18.15 (18.27)	30.68 (31.02)
$[(C_2H_4N_6O_2)CuSn_2Cl_4]$	205	Yellow	46	4.33 (4.48)	0.72 (0.83)	15.17 (15.29)	25.65 (25.99)
$[(C_2H_4N_6O_2)CuTi_2Cl_4]$	216	Orange	48	5.80 (5.96)	0.96 (1.06)	20.32 (20.43)	34.35 (34.88)
$[(C_2H_4N_6O_2)CuZr_2Cl_4]$	208	Orange	47	4.80 (4.93)	0.80 (0.92)	16.80 (16.93)	24.40 (24.98)
$[(C_2H_4N_6O_2)CuSn_2(CH3)_4]$	215	Orange	48	15.26 (15.38)	3.39 (3.46)	17.81 (17.96)	-

Table 1: contd.

Analytical data M.P. and yield of new heterobimetallic complexes of (2,2-amino, pyridyl thiazolidin-4 one)

Complexes	M.P. °C	Colour	Yield %	% Calcd. (Found)			
				C	H	N	Cl
$C_8H_9N_3SO$ (apt-H)	158	Cream	58	49.23 (49.63)	4.61 (4.73)	21.53 (21.74)	- -
$[Cu(apt\text{-}H)_2]Cl_2$	205	Brown	50	36.60 (36.96)	3.43 (3.56)	16.01 (16.23)	13.53 (13.83)
$[Zn(apt\text{-}H)_2]Cl_2$	208	Cream	50	36.46 (36.84)	3.41 (3.53)	15.95 (16.18)	13.41 (13.72)
$[Cu(apt)_2SiCl_2]Cl_2$	195	Yellow	48	30.89 (31.13)	2.57 (2.68)	13.51 (13.74)	22.84 (23.60)
$[Cu(apt)_2GeCl_2]Cl_2$	198	Yellow	45	28.82 (28.89)	2.40 (2.51)	12.61 (12.80)	21.31 (21.56)
$[Cu(apt)_2SnCl_2]Cl_2$	198	Yellow	45	26.98 (27.20)	2.24 (2.36)	11.80 (11.98)	19.95 (20.16)
$[Cu(apt)_2TiCl_2]Cl_2$	188	Yellow	46	29.93 (30.13)	2.49 (2.61)	13.09 (13.27)	22.12 (22.38)
$[Cu(apt)_2ZrCl_2]Cl_2$	185	Yellow		28.04 (28.34)	2.33 (2.41)	12.26 (12.39)	20.73 (20.93)

Table 1 contd.

Complexes	M.P. °C	Colour	Yield %	% Calcd. (Found)			
				C	H	N	Cl
$[Cu(apt)_2Sn(CH_3)_2]Cl_2$	188	Yellow	50	32.21 (32.48)	3.28 (3.33)	12.52 (15.70)	10.58 (10.77)
$[Zn(apt)_2SiCl_2]Cl_2$	193	Cream	43	30.72 (31.13)	2.56 (2.68)	13.42 (13.56)	22.17 (23.12)
$[Zn(apt)_2GeCl_2]Cl_2$	190	Cream	50	28.74 (28.98)	2.30 (2.43)	12.57 (12.69)	21.57 (21.83)
$[Zn(apt)_2SnCl_2]Cl_2$	188	Cream	48	26.91 (27.21)	2.24 (2.38)	11.77 (11.88)	19.90 (20.28)
$[Zn(apt)_2TiCl_2]Cl_2$	195	Cream	48	29.84 (30.13)	2.48 (2.59)	13.05 (13.29)	22.07 (23.38)
$[Zn(apt)_2ZrCl_2]Cl_2$	195	Cream	46	27.96 (28.16)	2.33 (2.40)	12.23 (12.41)	20.68 (20.96)
$[Zn(apt)_2Sn_2(CH3)_2]Cl_2$	188	Cream	48	32.12 (32.33)	3.27 (3.39)	12.49 (12.68)	10.55 (10.88)

Table 1 contd.

Complexes	M.P. °C	Colour	Yield %	% Calcd. (Found)			
				C	H	N	Cl
$[Cu(apt)_2Sn(CH_3)_2]Cl_2$	188	Yellow	50	32.21 (32.48)	3.28 (3.33)	12.52 (15.70)	10.58 (10.77)
$[Zn(apt)_2SiCl_2]Cl_2$	193	Cream	43	30.72 (31.13)	2.56 (2.68)	13.42 (13.56)	22.17 (23.12)
$[Zn(apt)_2GeCl_2]Cl_2$	190	Cream	50	28.74 (28.98)	2.30 (2.43)	12.57 (12.69)	21.57 (21.83)
$[Zn(apt)_2SnCl_2]Cl_2$	188	Cream	48	26.91 (27.21)	2.24 (2.38)	11.77 (11.88)	19.90 (20.28)
$[Zn(apt)_2TiCl_2]Cl_2$	195	Cream	48	29.84 (30.13)	2.48 (2.59)	13.05 (13.29)	22.07 (23.38)
$[Zn(apt)_2ZrCl_2]Cl_2$	195	Cream	46	27.96 (28.16)	2.33 (2.40)	12.23 (12.41)	20.68 (20.96)
$[Zn(apt)_2Sn_2(CH3)_2]Cl_2$	188	Cream	48	32.12 (32.33)	3.27 (3.39)	12.49 (12.68)	10.55 (10.88)

Table 2: Important IR absorptions data cm^{-1} of bis 1,3 diaminopropane zinc (II) Chloride and its heterobimetallic complexes

Complexes	ν NH	ν C-N ν C-C	δNH	ν MN	ν MCl
$[C_6H_{18}N_4Zn]Cl_2$	3480	3340 1340	1400	1575	-
$[C_6H_{14}N_4ZnSi_2Cl_4]$	3340	1440 1360	1575	422	285
$[C_6H_{14}N_4ZnGe_2Cl_4]$	3340	1443 1361	1575	516	330
$[C_6H_{14}N_4Zn\ Sn_2Cl_4]$	3340	1445 1362	1575	425	325
$[C_6H_{14}N_4Zn\ Ti_2Cl_4]$	3340	1440 1363	1575	430	320
$[C_6H_{14}N_4Zn\ Zr_2Cl_4]$	3340	1440 1360	1575	425	330
$[C_6H_{14}N_4Zn\ Sn_2(CH_3)_4]$	3340	1440 1360	1575	425	325

Table 2 Contd. : Important IR data of $[(scz)_2M]Cl_2$ and their heterobimetallic complexes

Complexes	νNH_2	$\nu C=O$	νNH	$\nu C-N$	δNH	νMN	νMCl
$[C_2H_{10}N_6O_2Cu]Cl_2$	3480	1650	3420	1440	1578	280	320
$[C_2H_4N_6O_2CuSi_2Cl_4]$	-	1650	3420	1440	1578	422	285
$[C_2H_4N_6O_2CuGe_2Cl_4$	-	1650	3420	1440	1578	516	330
$[C_2H_4N_6O_2CuSn_2Cl_4]$	-	1650	3420	1442	1578	425	325
$[C_2H_4N_6O_2CuTi_2Cl_4]$	-	1650	3420	1440	1578	430	320
$[C_2H_4N_6O_2CuSn_2(CH3)_4$	-	1650	3420	1444	1578	425	325
$[C_2H_{10}N_6O_2Zn]Cl_2$	3450	1650	3370	1440	1578	280	320
$[C_2H_4N_6O_2ZnSi_2Cl_4]$	-	1650	3370	1440	1578	422	285
$[C_2H_4N_6O_2ZnGe_2Cl_4$	-	1650	3370	1440	1578	516	330
$[C_2H_4N_6O_2ZnSn_2Cl_4]$	-	1650	3370	1442	1578	425	325
$[C_2H_4N_6O_2ZnTi_2Cl_4]$	-	1650	3370	1440	1578	430	320
$[C_2H_4N_6O_2ZnSn_2(CH3)_4$	-	1650	3370	1444	1578	425	325

Table 2

Complexes	νNH_2	νNH	$\nu C=O$	$\nu C-S$	$\nu C=N$	δNH	$\nu M-N$	$\nu M-Cl$
$C_8H_9N_3SO$ (apt-H)	3350	3150	1710	760	1640	1570	-	-
$[Cu(apt\text{-}H)_2]Cl_2$ (apt-H)	3220	3100	1710	730	1640	1440	285	230
$[Zn(apt\text{-}H)_2]Cl_2$	3230	3100	1710	760	1640	1440	280	240
$[Cu(apt)_2SiCl_2]Cl_2$	3230	3100	1710	760	1640	1440	285,430	325
$[Cu(apt)_2GeCl_2]Cl_2$	3230	3100	1710	760	1640	1440	285,516	330
$[Cu(apt)_2SnCl_2]Cl_2$	3230	3100	1710	760	1640	1440	285,425	325
$[Cu(apt)_2TiCl_2]Cl_2$	3230	3100	1710	760	1640	1440	285,420	325
$[Cu(apt)_2ZrCl_2]Cl_2$	3230	3100	1710	760	1640	1440	430,285	325
$[Cu(apt)_2Sn(CH_3)_2]Cl_2$	3230	3100	1710	760	1640	1440	285,420	-
$[Zn(apt)_2SiCl_2]Cl_2$	3230	3100	1710	760	1640	1440	280,430	330

$[Zn(apt)_2GeCl_2]Cl_2$	3230	3100	1710	760	1640	1440	280,430	330
$[Zn(apt)_2SnCl_2]Cl_2$	3230	3100	1710	760	1640	1440	280,425	330
$[Zn(apt)_2TiCl_2]Cl_2$	3230	3100	1710	760	1640	1440	280,420	330
$[Zn(apt)_2ZrCl_2]Cl_2$	3230	3100	1710	760	1640	1440	280,520	330
$[Zn(apt)_2Sn(CH3)_2]Cl_2$	3230	3100	1710	760	1640	1440	280,420	-

Table 3a: Percent mortality and LD_{50} of cockroaches with a corresponding concentration of 2,2 amino,pyridyl - thiazolidin-4- one (apt-H)

Complex	Log concentration in ppm x 100	% Mortality	Probit value	LD_{50}
apt-H	2.00	10	3.7184	
	2.30	20	4.1584	
	2.47	30	4.4756	4.89
	2.60	40	4.7467	
	2.69	50	5.0000	
$[(apt\text{-}H_2Cu)]Cl_2$	2.00	20	4.1584	
	2.30	30	4.4756	
	2.47	40	4.7467	3.98
	2.60	50	5.0000	
	2.69	60	5.2533	
$[Cu(apt\text{-}H)_2SnCl_2]Cl_2$	2.00	30	4.4756	
	2.30	40	4.7467	
	2.47	50	5.0000	2.91
	2.60	60	5.2533	
	2.69	70	5.5244	

Table 3b: Percent inhibition data (a) A. niger (b) A. flavus (c) A. pori

Complex	Concentration	% inhibition
(a) apt-H	2.00	60
	2.50	65
	3.00	70
$[(apt\text{-}H)_2Cu]Cl_2$	2.00	65
	2.50	70
	3.00	75
$[Cu\ (apt)_2SnCl_2]Cl_2$	2.00	70
	2.50	75
	3.00	80
(b) apt-H	2.00	64
	2.50	68
	3.00	71
	2.00	68
$[(apt\text{-}H)_2Cu]Cl_2$	2.50	76
	3.00	75
$[Cu(apt)_2\ \ SnCl_2]Cl_2$	2.00	75
	2.50	79
	3.00	80
(c) apt-H	2.00	65
	2.50	68
	3.00	70
$[(apt\text{-}H)_2Cu]Cl_2$	2.00	68
	2.50	76
	3.00	78
$[Cu(apt)_2\ SnCl_2]Cl_2$	2.00	75
	2.50	78
	3.00	80

CHAPTER IV

(A) HETEROBIMETALLIC CHELATES OF 2-AMINO-3 FORMYL CHROMONE AND ITS SCHIFF BASE

CHAPTER IV(A)

HETEROBIMETALLIC CHELATES OF 2-AMINO-3-FORMYLCHROMONE AND ITS SCHIFF BASE

EXPERIMENTAL

Hydrated Cu(II), Ni(II) chlorides and 1,3-diamino propane (E.Merck), Si(IV), Ge(IV), and Sn(IV) tetrachlorides (Fluka) were used as such. Solvents were distilled and dried by conventional methods. Microanalyses were performed on Perkin-Elmer 240-B microanalyser, IR spectra were run on a Perkin Elmer 240 FT spectrophotometer in KBr and Nujol. The UV/visible and EPR spectra were recorded on a Pye Unicam PU8800 spectrophotometer and BRUKER ESP-300 X-band spectrometer, respectively. ^{1}H NMR spectra were run on a BRUKER WP80 SY spectrometer. The conductivity measurements were made on an Elico conductivity bridge type CM-82T.

Synthesis of 2-amino-3-formyl chromone (afc)

It was synthesised by the literature method.[88]

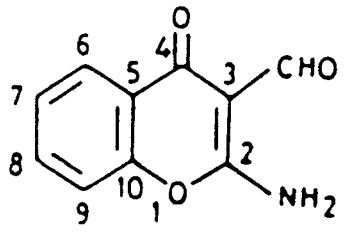
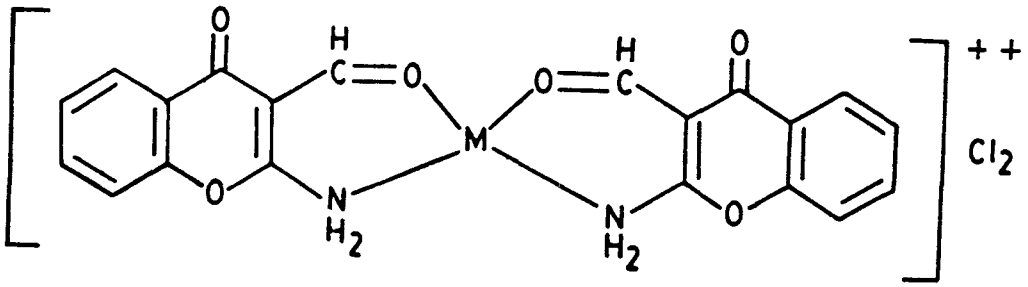


Fig. 19

Synthesis of the complexes of chromone, $[(afc)_2M]Cl_2$

To the solution of chromone (0.002 mol, 0.382g) in ethanol (25 mL) was added hydrated copper(II) chloride (0.001 mol, 0.171g) or nickel(II) chloride (0.001 mol, 0.290g) and refluxed for ca.10 h. After standing this mixture at room temperature for a few days a crystalline solid was obtained which was filtered and dried in vacuo.

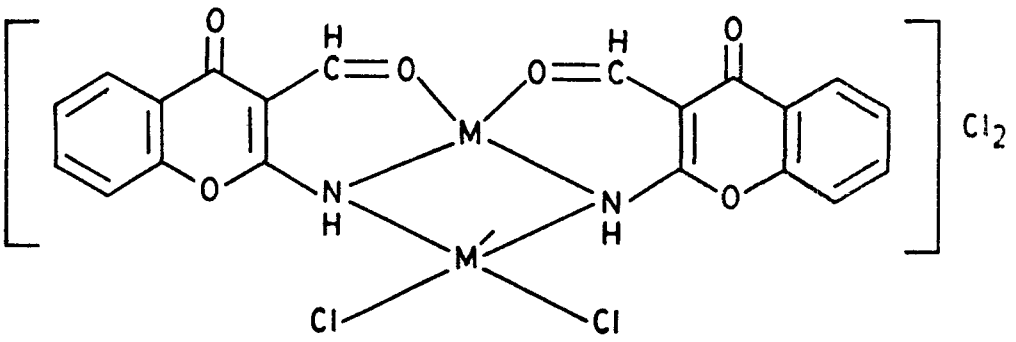


M = Cu, Ni(II)

Fig.20

Synthesis of bimetallic complexes of afc $[M\ (afc)_2M'Cl_2]Cl_2$

A mixture of $[(afc)_2M]Cl_2$ (0.001 mol) and the Group IV metal tetrachloride (0.001 mol) were taken in a 100 mL round bottom flask in dry methanol (30 mL) and was refluxed for 3-4 h. It was set aside for 20 days' at room temperature until a crystalline compound separated out. The crystals were filtered and dried *in vacuo*.



M´ = Si, Ge, Sn, Ti, Zr (IV)

Fig.21

Synthesis of the Schiff base ($SB-H_2$)

To a solution of 2-amino-3-formylchromone (0.002 mol, 0.38g) in ethanol (30 mL) was added 1,3-diamino propane (0.001 mol, 0.098 mL). The resulting mixture was refluxed for 3 h and refrigerated for 8 h when orange crystals of the Schiff base ($SB-H_2$) separated out. It was washed with hexane and dried in vacuo.

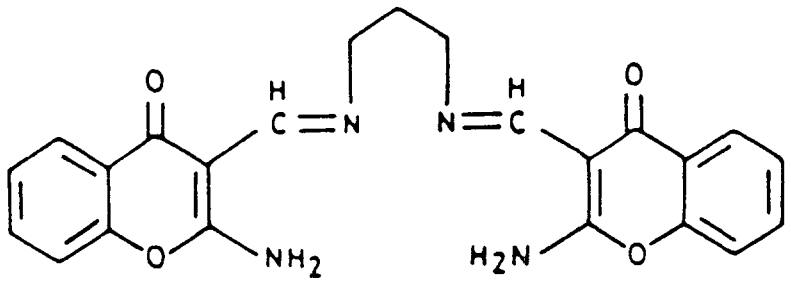


Fig.22

Synthesis of the Schiff base complexes, $[M(SB\text{-}H_2)]Cl_2$

To the solution of Schiff base ($SB\text{-}H_2$) (0.001 mol, 0.416 g) in ethanol (30 mL) was added hydrated copper(II) chloride (0.001mol, 0.170g) or nickel(II) chloride (0.001 mol, 0.237g) and refluxed for ca 10 h. After standing this mixture at room temperature for a few days, a crystalline solid was obtained which was filtered off and dried in vacuo.

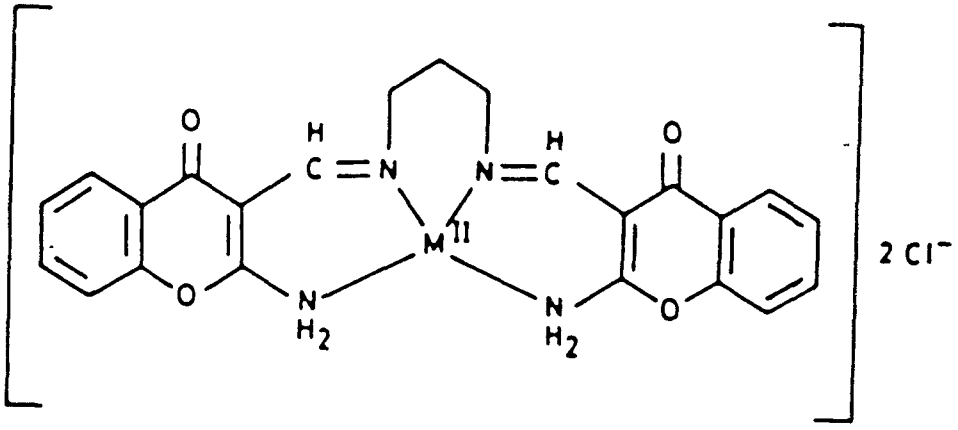


Fig.23

Synthesis of bimetallic complexes, $[M\ (SB)M'Cl_2]Cl_2$

The complex $[Ni\ (SB\text{-}H_2)]Cl_2$ (0.001 mol, 0.54g) or $[Cu(SB\text{-}H_2)]Cl_2$ (0.001 mol, 0.55g) was further refluxed with Group (IV) tetrachlorides (0.001 mol) in dry MeOH (30 mL) for 3-4 h to achieve bimetallic complexes. Since no immediate reaction occurred the mixture was left for about 20 days at room temperature when crystalline compounds separated out which were filtered and dried in vacuo. (Table 4).

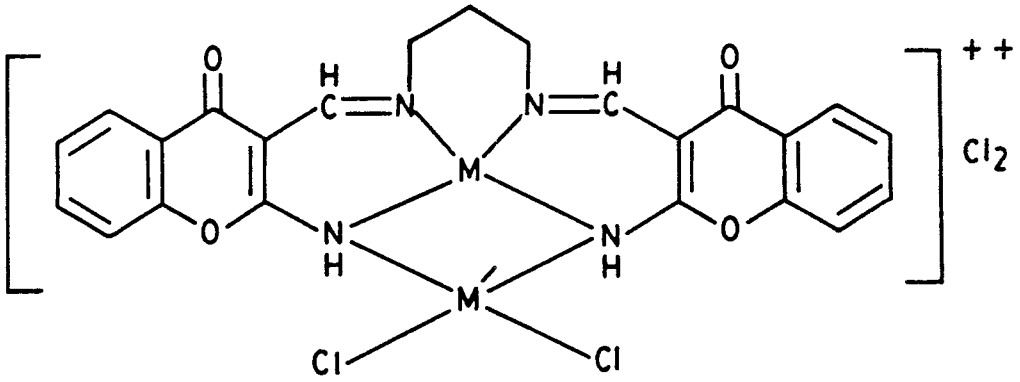


Fig.24

RESULTS AND DISCUSSION

2-Amino-3-formylchromone acts as a quadridentate N_2O_2 ligand. The complexes are formed according to the equations:

$$MCl_2 + 2\ afc \xrightarrow[reflux]{EtOH} [(afc)_2\ M]Cl_2$$

$$[(afc)_2M]Cl_2 + MCl_4 \xrightarrow[reflux]{Dry\ MeOH} [M(afc)_2M'Cl_2]Cl_2 + 2HCl$$

$$afc + H_2N(CH_2)_3NH_2 \xrightarrow[-2H_2O]{EtOH/reflux} \text{Schiff base } [SB\text{-}H_2]$$

$$SB\text{-}H_2 + MCl_2 \xrightarrow{EtOH} [M(SB\text{-}H_2)]Cl_2$$

$$[M(SB\text{-}H_2)]Cl_2 + M'Cl_4 \xrightarrow[-2HCl]{Dry\ EtOH} [M(SB)M'Cl_2]Cl_2$$

afc = 2 amino-3-formyl chromone

M = Cu(II), Ni(II) M' = Si(IV), Ge(IV), Sn(IV) and Zr(IV).

The IR spectra

In the free chromone two medium and broad absorptions corresponding to ν NH at 3100 and 3250 cm^{-1} have been noted. It has been reported by Ferrari et al[89] that pyridoxal thiosemicarbazone shows NH_2 absorptions at 3380 cm^{-1}. Since our spectrum was run in KBr, the hydrogen bonding lowered the

NH frequency. A very sharp and strong band at 1625 cm^{-1} has been observed and assigned to C=O stretching vibration which is supported by the observation made by Srimannarayana[37] on 2-styrylchromone. It is difficult to distinguish between a ketonic ν(C=O) and an aldehydic ν(C=O) group because they absorb in the same region of the spectrum. We have, however, identified the aldehydic ν C=O as a medium strong band at 1665 cm^{-1} which is consistent with the observation made by Casellato and coworkers.[90]

The complexes of 2-amino-3-formyl chromone with Cu(II) and Ni(II) show NH stretching frequencies at 3249 cm^{-1} and 3500 cm^{-1} respectively, which are characteristics of NH_2 group. A band at 1625 cm^{-1} assigned to ν C=O (ketonic) remains nearly unaltered indicating its noninvolvement in coordination. However, aldehydic C=O (1665 cm^{-1}) has been observed to show a significant change as compared to free chromone (Table 5) indicating the coordination of formyl oxygen with the metal ion. Two medium intensity bands at 1511 cm^{-1} and 1572 cm^{-1} due to vibration of the heterocyclic ring also remained unaltered.[91] A strong absorption band at 1339 cm^{-1} has been identified as NH_2 deformation mode.

The spectra of bimetallic complexes exhibited a broad peak at 3400 cm^{-1} which has been assigned to ν NH. Since the

coordination of the Group(IV) metals occurs through amino nitrogen by the replacement of a proton from NH_2, a shift in NH occurred making the Group IV atom four coordinated (Fig.21). The bands appearing at 425, 385, 340, 335, and 295 cm^{-1} have been assigned to ν M-O, ν M-N and ν M-Cl, respectively. The spectral data of the complexes suggest that aldehydic oxygen and amino nitrogen are coordinated to the metal ions. Besides, the (cyclic) ν C-O, (exocyclic)ν C=O and symmetric ring vibrations remain unaltered.

IR Spectra of Schiff base ($SB-H_2$) and its complexes

The Schiff base of (afc) shows a broad band at 3100cm^{-1} due toνNH. A shoulder at 1662 cm^{-1} has been ascribed to ν C=N of the azomethine[93] group since ν C=O is replaced by C=N in the formation of Schiff base. The Cu(II) and Ni(II) complexes with Schiff base show sharp bands in the 1648-1662 cm^{-1} range which are assigned to ν C=N, these bands are lowered by ca 10-40cm^{-1} indicating coordination through azomethine nitrogen atoms. It appears from the structure (Fig.23) that ketonic ν C=O and ν C-O are not involved in coordination which is evidenced by persistent appearance of ketonicν C=O at about 1615-1620 cm^{-1} in the free Schiff base and its complexes with Cu(II), Ni(II) and also their bimetallic chelates with Group IV tetrachlorides.

The complexes are formed by the substitution of a proton in the 2-amino-3- formyl chromone at position 2 leading to the formation of a Group IV metal nitrogen covalent bond. There is an equal possibility of bonding the metal through the nitrogens at position 2 and the ring oxygen on either side but the analytical data do not support this composition. The elemental analysis and the spectral results (Table 6,7) indicate that only one Group IV metal is bonded to both the amino nitrogens of chromone at position 2 making the metal distorted tetrahedral.

NMR Spectrum of free chromone

The NMR spectrum of 2-amino-3-formyl chromone recorded in DMSO-d_6, shows one singlet at δ 10.10 and another singlet at δ 9.60 which have been ascribed to aldehydic and NH protons, respectively. Aromatic proton signals have been observed in δ 7.36 to 8.06 which is in consonance with the results obtained by Srimannarayana et al on the chromone derivatives.[37]

Electronic spectra

The electronic spectrum in ethanol shows absorptions mainly in the UV region. The peaks at 37037 and 33333 cm^{-1} due to $n \rightarrow \pi^*$ transitions have been assigned to aldehydic and ketonic C=O in free chromone.

The two d-d transitions in Ni(II) complex observed at 14085 and 21978 cm^{-1} are assignable to dxz, dyz, dxy and $dx^2 \rightarrow y^2$ respectively. The absence of any other band below 14000 cm^{-1} are characteristics of the Ni(II) ions in the square planar environment. In the case of Cu(II) complex a charge transfer band at 27,277 cm^{-1} has been observed. The magnetic moment value (1.65 BM) is slightly less than calculated for one electron (1.73 BM) but well within the range of a square planar geometry for Cu(II) ion.

The EPR spectrum of $(afc)_2CuCl_2$ ($g_{\perp}$ 2.02 and g_{11} 2.13) indicates that the Cu(II) ion has square planar geometry.[94] Our results are consistent with those reported by Hathaway and coworkers[95] on Cu(II) complex with square planar geometry.

TABLE 4: Analytical data of 2-amino-3-formylchromone and its complexes

Complex	Colour	M.P.(°C)	%Analyses cald.(found)			Yield %
			C	H	N	
$C_{10}H_7O_3N$ (afc)	Brown	252	53.69 (53.12)	3.13 (3.23)	6.26 (6.37)	65
$[(C_{10}H_7O_3N)_2Cu]Cl_2$	Grey	>300d	46.96 (46.90)	2.76 (2.70)	5.47 (5.41)	65
$[(C_{10}H_7O_3N)_2Ni]Cl_2$	Dark brown	280	47.36 (47.86)	2.76 (2.86)	5.52 (5.54)	63
$[(C_{10}H_6O_3N)_2CuSiCl_2]Cl_2$	Cream	265	40.00 (40.50)	2.00 (2.10)	4.64 (4.68)	40
$[(C_{10}H_6O_3N)_2CuGeCl_2]Cl_2$	Orange	240	36.68 (36.88)	1.84 (1.85)	4.28 (4.30)	40
$[(C_{10}H_6O_3N)_2CuSnCl_2]Cl_2$	Cream	225	34.27 (34.47)	1.72 (1.73)	3.99 (4.10)	45
$[(C_{10}H_6O_3N)_2NiSiCl_2]Cl_2$	Yellow	230	39.81 (39.90)	1.99 (2.00)	4.64 (4.67)	40
$[(C_{10}H_6O_3N)_2NiGeCl_2]Cl_2$	Yellow	240	37.07 (37.17)	1.85 (1.95)	4.32 (4.35)	38
$[(C_{10}H_6O_3N)_2NiSnCl_2]Cl_2$	Light Yellow	235	34.61 (34.71)	1.73 (1.82)	4.03 (4.08)	35

TABLE 5 : Important IR absorption cm^{-1} of 2-amino-3-formyl chromone and its complexes

Complex	νNH cm^{-1}	νC=O cm^{-1}	δNH & CH cm^{-1}
$C_{10}H_7O_3N$ (afc)	3100,3250	1625,1665	1320,1465
$[(C_{10}H_7O_3N)_2Cu]Cl_2$	3249,3500	1615,1652	1339,1385
$[C_{10}H_7O_3N)_2Ni]Cl_2$	3144,3444	1615,1650	1300,1353
$[(C_{10}H_6O_3N)_2CuSiCl_2]Cl_2$	2945,3400	1618,1650	1353,1350
$[(C_{10}H_6O_3N)_2CuGeCl_2]Cl_2$	2950,3400	1615,1650	1352,1264
$[(C_{10}H_6O_3N)_2CuSnCl_2]Cl_2$	2950,3400	1618,1650	1352,1264
$[(C_{10}H_6O_3N)_2NiSiCl_2]Cl_2$	2968,3400	1615,1652	1350,1253
$[(C_{10}H_6O_3N)_2NiGeCl_2]Cl_2$	2950,3400	1618,1650	1360,1260
$[(C_{10}H_6O_3N)_2NiSnCl_2]Cl_2$	2950,3400	1615,1650	1360,1260

TABLE 6 : Analytical data of chromone Schiff base and its complexes

Complex	Colour	M.P.(^{o}C)	%Analyses cald. (found)		
			C	H	N
$C_{23}H_{20}O_4N_4$(SB-H_2)	Orange	198	66.30 (66.70)	4.80 (4.86)	13.46 (13.56)
$[C_{23}H_{20}O_4N_4Cu]Cl_2$	Brown	>300 d	50.18 (50.45)	3.63 (3.71)	10.18 (10.28)
$[C_{23}H_{20}O_4N_4Ni]Cl_2$	Dark brown	>300 d	50.56 (50.90)	3.66 (3.73)	10.26 (10.38)
$[C_{23}H_{18}O_4N_4CuSiCl_2]Cl_2$	Cream	210	42.72 (42.98)	2.78 (2.98)	8.66 (8.73)
$[C_{23}H_{18}O_4N_4CuGeCl_2]Cl_2$	Orange	225	39.70 (39.90)	2.60 (2.70)	8.79 (7.68)
$[C_{23}H_{18}O_4N_4CuSnCl_2]Cl_2$	Cream	220	37.44 (37.80)	2.44 (2.60)	7.56 (7.68)
$[C_{23}H_{18}O_4N_4CuZrCl_2]Cl_2$	Yellow	230	38.76 (38.90)	2.53 (2.63)	7.88 (7.99)
$[C_{23}H_{18}O_4N_4NiSiCl_2]Cl_2$	Cream	215	42.93 (43.30)	2.70 (2.82)	8.71 (8.83)
$[C_{23}H_{18}O_4N_4NiGeCl_2]Cl_2$	Orange	230	40.14 (40.44)	2.61 (2.65)	8.14 (8.24)
$[C_{23}H_{18}O_4N_4NiSnCl_2]Cl_2$	Pale Yellow	225	37.66 (37.86)	2.45 (2.50)	7.64 (7.77)
$[C_{23}H_{18}O_4N_4NiZrCl_2]Cl_2$	Yellow	240	39.09 (39.39)	2.54 (2.64)	7.93 (7.99)

TABLE 7 : IR Spectral data of the chromone Schiff base and its complexes

Complexes	ν NH cm^{-1}	ν C=O cm^{-1}	ν C=N cm^{-1}	ν C-C cm^{-1}
$C_{23}H_{20}O_4N_4$ (SB-H_2)	3100	1620	1662	1562
$[C_{23}H_{20}O_4N_4]CuCl_2$	3244	1615	1658	1510
$[C_{23}H_{20}O_4N_4]NiCl_2$	3248	1615	1652	1520
$[C_{23}H_{18}O_4N_4CuSiCl_2]Cl_2$	3248	1618	1652	1511 1571
$[C_{23}H_{18}O_4N_4CuGeCl_2]Cl_2$	3240	1618	1652	1518 1570
$[C_{23}H_{18}O_4N_4CuSnCl_2]Cl_2$	3249	1618	1658	1515 1570
$[C_{23}H_{18}O_4N_4CuZrCl_2]Cl_2$	3248	1618	1652	1500 1570
$[C_{23}H_{18}O_4N_4NiSiCl_2]Cl_2$	3240	1615	1658	1511 1572
$[C_{23}H_{18}O_4N_4NiGeCl_2]Cl_2$	3244	1618	1662	1511 1570
$[C_{23}H_{18}O_4N_4NiSnCl_2]Cl_2$	3249	1620	1658	1511 1575
$[C_{23}H_{18}O_4N_4NiZrCl_4]Cl_2$	3250	1618	1652	1510 1570

(B) NOVEL HETEROBIMETALLIC CHELATES; CONDENSATION OF (3-ACETOACETYL-7-METHYL-PYRANO-(4,3-b)-PYRAN-2, 5-DIONE)AND (1-NITRO-2,2, BIS (METHYL THIO ETHYLENE) WITH BIS-1,3-DIAMINO-PROPANE Ga(II) CHLORIDE AND GROUP IV METAL TETRACHLORIDES

CHAPTER -IV (B)

NOVEL HETEROBIMETALLIC CHELATES: CONDENSATION OF (3-ACETOACETYL-7-METHYL-PYRANO-(4,3-b)-PYRAN-2, 5-DIONE) AND (1-NITRO-2, 2, BIS (METHYL THIO ETHYLENE) WITH BIS-1,3-DIAMINOPROPANE Cu(II) CHLORIDE AND GROUP IV METAL TETRACHLORIDES.

EXPERIMENTAL

Hydrated Cu(II) chloride, carbondisulphide, potassium hydroxide (BDH) 1,3-diaminopropane (E.Merck), Si(IV), Ge(IV), Sn(IV), Ti(IV), Zr(IV) chlorides, dimethyl tin-, and diethyl tindichloride, dimethylsulphate and nitromethane (Fluka) were used as received. Microanalyses were performed on a Perkin Elmer 240-B micro-analyser. IR spectra were recorded on a Perkin Elmer 240 FT spectrophotometer as KBr discs. Far IR spectra were recorded on a Perkin Elmer 621 spectrophotometer in Nujol. The UV-visible and EPR spectra were recorded on a Pye Unicam PU8800 spectrophotometer and Bruker ESP-300 X-band spectrometer, respectively. The ^{1}H and ^{13}C NMR were run on Bruker WP 80 SY spectrometer. The conductivity measurements were made on an Elico conductivity bridge type CM-82T.

Toxic Effect

Toxicity experiments were done on cockroaches (Periplaneta americana). The concentrations of the complexes were kept between 8-12 ppm region. The percent mortality after 24 and 96 h was noted. The LD_{50} was calculated in terms of probit.[85] Fungitoxicity[84] was also evaluated against A.niger, A.Flavus and A.pori. They were treated with a 2-3% solution of the compounds and the results were compared against an untreated set under the same experimental conditions. The per cent inhibition in growth was calculated.

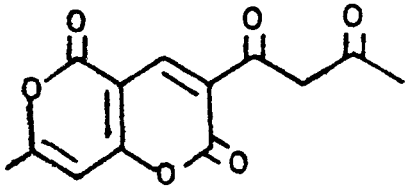
Synthesis of [3acetoacetyl-7-methyl-pyrano-(4,3-b)-pyran-2, 5-dione) (L_1)

4-Hydroxy-6-methyl-2H-pyran-2-one (0.01 mol, 1.0g) was added in portions to a preheated mixture of moist ethyl orthoformate (0.01 mol, 10 mL) containing traces of p-toluene sulphonic acid. The reaction mixture was heated for another 15 minutes and cooled to $10^{o}C$ when a yellow crystalline solid precipitated. It was recrystallised from chloroform.

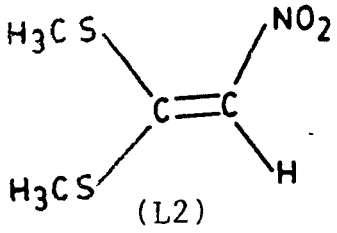
Synthesis of of [1-nitro-2,2 bis methyl thio ethylene] (L_2)

Carbondisulphide (0.01 mol, 0.60 mL) was added dropwise to nitromethane (0.01 mol, 0.540 mL) in 20 mL absolute ethanol in presence of concentrated alcholic KOH at $5^{o}C$. A crystalline solid separated out immediately on further

cooling.[96-97]. Reaction of this solid with dimethyl sulphate in MeOH-H_2O mixture at 10°C afforded a white precipitate after stirring for ca. 5h. The product was recovered by adding 300 ml of H_2O and recrystallised from MeOH.



(L1)



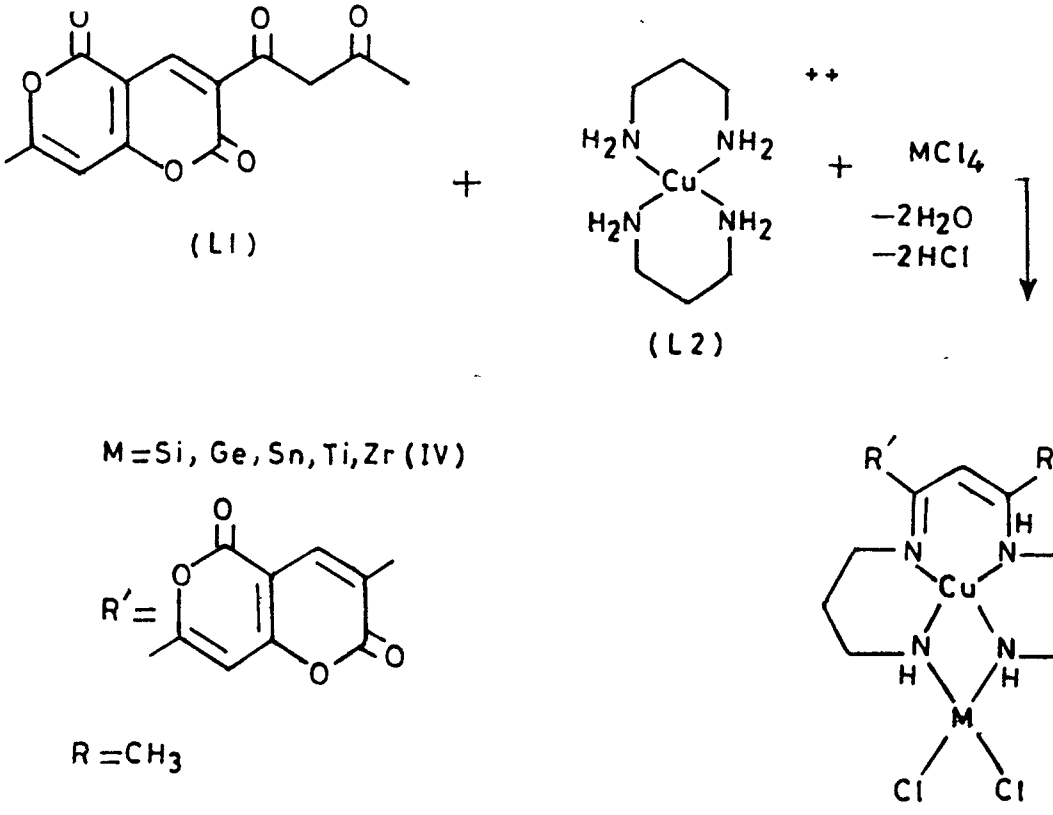
(L2)

L_1 = [3-acetoacetyl-7-methyl(4,3-b)pyran-2,5-dione]

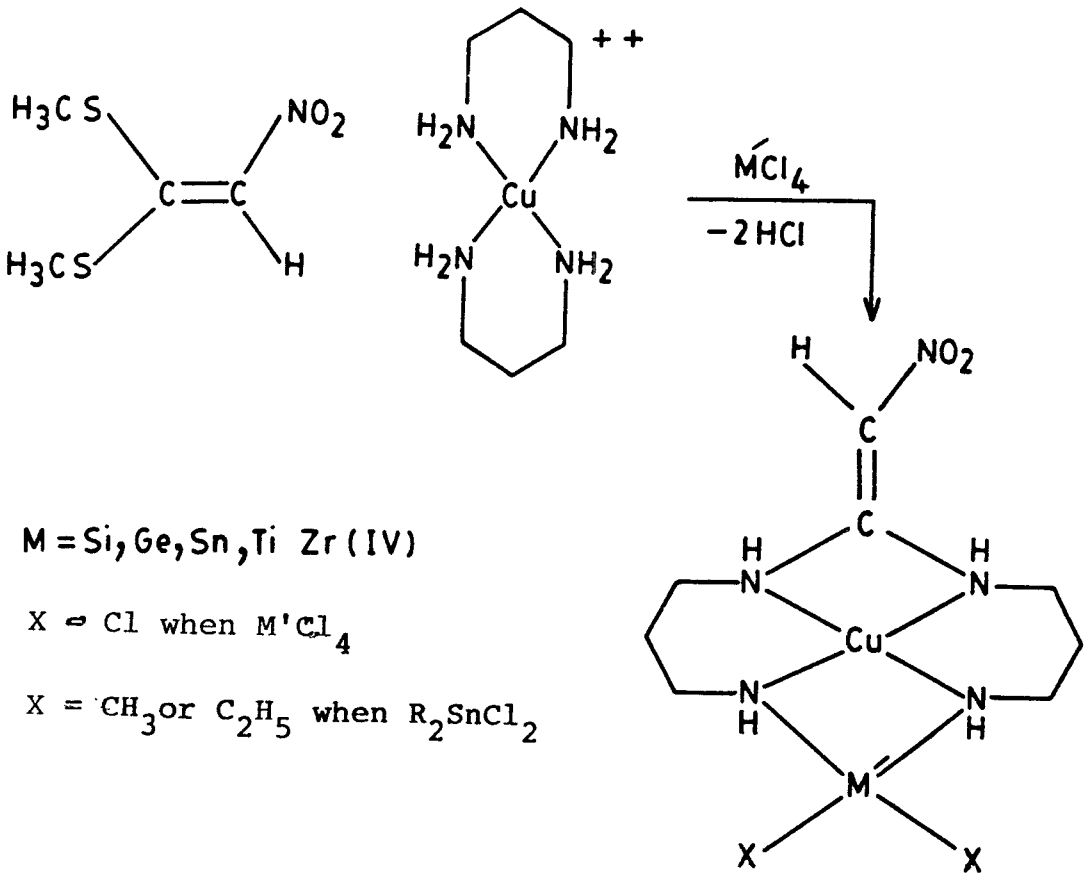
L_2 = [1-nitro-2,2-bis (methyl thio) ethylene]

Fig.25

SCHEME I



SCHEME - II



M = Si, Ge, Sn, Ti Zr (IV)

X = Cl when $M'Cl_4$

X = CH_3 or C_2H_5 when R_2SnCl_2

Synthesis of bis [1,3-diaminopropane] Copper(II) chloride $[Cu(dap)_2]Cl_2$

Bis(1,3-diaminopropane) Cu(II) chloride was prepared by refluxing a mixture of hydrated cupric chloride (0.01 mol, 1.71 g) and 1,3-diaminopropane (0.02 mol, 1.58 mL) in 50 mL ethanol for 1 h. Blue crystals were separaed on standing the liquid for 12 h at room temperature. They were recrystallised from ethanol and dried *in vacuo*.

Synthesis of complexes

A hot solution of L_1 (0.01 mol, 2.62 g) or L_2' (0.01 mol, 1.61 g) in dry methanol (20 mL) was mixed with $[Cu(dap)_2]Cl_2$ (0.01 mol, 2.26 g) in presence of Group(IV) metal tetrachlorides or diorganotindichloride(0.01 mol) and refluxed for 2-3 h when this dark red mixture turned yellowish brown. After cooling it to room temperature 10 mL hexane was cautiously added without disturbing the solution and left for *ca* 6 days when it yielded fine crystals. They were dried in vacuo.

$$L_1 + [Cu(dap)_2]Cl_2 \xrightarrow[\text{reflux}]{MCl_4} [Cu(SB)M'Cl_2]Cl_2$$

$$L_2 + [Cu(dap)_2]Cl_2 \longrightarrow [Cu(L_{*2})\ M'Cl_2]Cl_2$$

RESULTS AND DISCUSSION

The ligand L_1 has been characterized by ^1H NMR, ^{13}C NMR, IR, UV and mass spectral data.

$IR(KBr)_{max}$: 1760, 1725, 1687, 1626, 1555s and 1198 cm^1

^1H NMR (90 MHz); 2.2(3H, s, $-C-CH_3$); 2.3(3H, s,$-C-CH_3$)
6.2(1H, s, -C-CH-); 6.7(1H, s,-C=CH-C-)
8.7(1H, s, -C-C-CH=C-C-).

^{13}C NMR : C_1-C_{13} 21.013, 27.460, 76.678, 76.996, 77.313, 98.852, 100.900, 159.4, 142.662, 171.049, 168.471, 199.468.

UV(MeOH) $_{max}$: 215, 280 and 400 nm

Mass(rel.int) : m/z 262(M^+,37), 247(14), 220(20), 219(4), 205(100, 150(13), 85(20).

All the complexes are air stable. Molar conductance of their millimolar solutions in DMSO (70-85 $ohm^{-1}cm^2mol^{-1}$) indicated them to be 1:2 electrolyte.

IR Spectra

Since L_1 contains both C-O and C=O bands different frequencies are expected for them. The L_1 shows two prominent bands at 1760 and 1725 cm^{-1} which have been assigned to ketonic ν C=O. Well defined absorption bands at 1687, 1626, 1555 cm^{-1} have been assigned to exocyclic νC=O. In the

absence of any other functional group the lower frequency band at 1198 cm^{-1} is assigned to heterocyclic C-O although its coupling with other bands is also likely. The spectrum of L_2 shows two strong absorption bands at 760 cm^{-1} and 1540 cm^{-1} which has been assigned to ν C-S and NO_2 stretching vibrations, respectively. The spectrum of $[Cu(dap)_2]Cl_2$ shows sharp bands at 3176, 3321, 3305 cm^{-1} due to νNH_2. The bands at 1575 cm^{-1}, 1148-1400 cm^{-1} have been assigned to δ NH, ν C-N and ν C-C respectively.

When L_1 or L_2 react with $[Cu(dap)_2]Cl_2$ in presence of MCl_4 (or R_2SnCl_2) M-N bond is formed by replacement of one H from NH_2 of 1,3-diaminopropane. A change from NH_2 (3176, 3321, 3395 cm^{-1}) to NH (3094-3181 cm^{-1}) accompanied by chelation with Group(IV) metal atom causes a substantial shift of <u>ca</u> 80 cm^{-1} (Table-9). The Schiff base complex formation leads to the formation of C=N bond which is supported by the emergence of a new band in 1609-1616 cm^{-1} region. Consequently, δ NH is observed in 1585-1590 cm^{-1} range, however, all other frequencies viz. ν C-C, ν C-N, νC=C, νC=O (exocyclic), ν C-O (cyclic) and ν NO_2 remain almost unchanged suggesting that coordination occurs only through the nitrogen atoms of the ligand. This observation is in consonance with the results reported earlier in the case of

unsymmetrical or symmetrical dinuclear Cu(II) Schiff base complexes.[98-99]

In the far IR region two strong bands at 510 cm^{-1} and 280 cm^{-1} have been attributed to ν Sn-C and ν Cu-N respectively.[100] New bands of medium intensity lying at 440,430, 425, 430 cm^{-1} have been identified as ν(Si-N), ν(Ge-N), ν(Sn-N), ν(Ti-N) and ν(Zr-N) modes respectively. The ν M-Cl also appear in the same region although they are stronger than ν M-N. It is clear from these studies that of all the potential sites only those containing nitrogen atom take part in coordination.

UV Spectrum

In the free L_1 strong n-π^*,$\pi-\pi^*$ bands are observed at 215, 280 and 400 nm and their intensities increase greatly upon condensation with bis (1,3-diamino propane) copper(II) chloride in presence of Group IV metal chloride. The weak absorption band observed at 360 nm is associated with the conjugation of (C=N) of Schiff base system. This observation provides further evidence for coordination taking place through the nitrogen atoms.

Electronic Spectra

Electronic spectra of bimetallic complexes in DMSO show weak d-d transitions in the region 16126-18248 cm^{-1}. In

addition, the spectra show bands of medium intensity at 33222 cm^{-1} assigned to L ----> M charge transfer. The visible spectra show bands at 16126, 16977 and 18248 cm^{-1} corresponding to A_{1g} <---- B_{1g}, B_{2g} <--- B_{1g} and E_g <---B_{1g} transitions, respectively as expected for copper(II) complexes with square planar geometry.[101-102] This is further supported by e.s.r. data g_{II} (2.13), and $g_{\perp}$(2.02) and the low magnetic moment value (1.40 BM) which may be due to diamagnetic effect in a bimetallic tetradentate Schiff base complex.

Toxicity

The compounds containing -C=O and $-CH_3$ have inherent fungicidal property and hence it seemed essential to investigate their toxicity against insects and fungi (Table 10). It has been observed that the complexes are better growth inhibitor for fungi than the free ß-diketone. These heterobimetallic complexes may thus be promising as fungicides.

Table 8: Analytical data, M.P., colour and molar conductance (Λ_m) of heterobimetallic complexes.

Complexes	M.P. °C	Colour	% Calcd. (Found)				ohm^{-1} cm^2 mol^{-1}	% Yield
			C	H	N	Cl		
$[C_{13}H_{10}O_6]$ (L1)	262	Orange	59.53 (58.66)	3.84 (3.90)	-	-	-	
$[C_6H_{20}N_4Cu]Cl_2$	260	Blue	25.48 (25.58)	7.07 (7.16)	19.82 (19.92)	-	70	40
[Cu(SB) $SiCl_2$]Cl_2	175	Yellow	36.60 (36.90)	3.95 (3.98)	9.32 (9.42)	-	72	45
[Cu(SB) $GeCl_2$]Cl_2	170	Yellow	35.07 (35.38)	3.69 (3.73)	8.61 (8.74)	-	74	45
[Cu(SB) $SnCl_2$]Cl_2	160	Brown	32.74 (32.88)	3.43 (3.49)	8.04 (8.14)	20.11 (20.31)	55	75
[Cu(SB) $TiCl_2$]Cl_2	165	Brown	36.53 (36.68)	3.84 (3.94)	8.97 (9.10)	-	75	43
[Cu(SB) $ZrCl_2$]Cl_2	>300d	Dark yellow	34.09 (34.29)	3.58 (3.69)	8.37 (8.48)	-	70	42
[Cu(SB) $Sn(CH_3)_2$]Cl_2	1142	Brown	38.53 (38.70)	4.58 (4.69)	8.55 (8.67)	13.24 (13.28)	70	42
[Cu(SB) $Sn(C_2H_5)_2$]Cl_2	165	Brown	40.47 (40.60)	4.98 (5.10)	8.20 (8.31)	-	50	42

SB = $C_{19}H_{24}N_4O_4$ d = decompose

Table 8 contd.

Complexes	M.P. °C	Colour	Yield %	% Calcd. (Found) C	H	N	Cl	ohm^{-1} cm^2 mol^{-1}
$C_4H_7NS_2O_2$ L2	125	Brown	60	29.81 (29.96)	4.34 (4.45)	8.69 (8.79)	-	
$[Cu(L_2)SiCl_2]Cl_2$	218	Yellow	30	21.50 (21.84)	3.35 (3.43)	15.67 (15.80)	(37.80) (38.20)	76
$[Cu(L_2^*)GeCl_2]Cl_2$	235	Orange	35	19.55 (19.86)	3.05 (3.14)	14.25 (14.35)	28.29 (29.26)	73
$[Cu(L_2^*)SnCl_2]Cl_2$	230	Brown	40	17.87 (18.12)	2.79 (2.81)	13.03 (13.26)	26.44 (27.30)	73
$[Cu(L_2^*)Sn(CH3)_2]Cl_2$	225	Brown	38	24.19 (24.93)	4.23 (4.36)	14.11 (14.23)	14.31 (14.81)	78
$[Cu(L_2^*)Sn(C_2H_5)_2]Cl_2$	220	Dark orange	38	27.48 (28.13)	4.77 (4.89)	13.35 (13.46)	14.08 (14.68)	77
$[Cu(L_2^*)TiCl_2]Cl_2$	260	Yellow	38	20.60 (21.10)	3.20 (3.33)	15.02 (15.15)	30.47 (30.98)	78
$[Cu(L_2^*)ZrCl_2]Cl_2$	263	Yellow	40	21.88 (22.02)	3.41 (3.58)	15.95 (16.03)	32.37 (32.97)	78

$L_2^* = C_8H_{15}N_5O_2$

Table 9: IR spectral data of the ligands L1, L2 and their heterobimetallic complexes with Group IV metal chloride.

Complex	νNH	ν NH	ν C=O	ν C=N	ν C=O	ν C-O	ν C-C	δ NH	ν M-C	νM-N
$[C_{13}H_{10}O_6]$ (L1)	-	-	1725s 1760s 1760s	-	1687s	1198s	-	-	-	-
$[C_6H_{20}N_4]$ (L2)	3176b 3325s 3395b	-	-	-	-	-	1148m 1400m	1575m	-	280s
[Cu(SB) $SiCl_2$]Cl_2	-	3094b 3181b	-	1616s	1687m	1198s	"	1585	-	440w
[Cu(SB) $GeCl_2$]Cl_2		"		1609s	1687m	1198s	"	1588	-	430w
[Cu(SB) $SnCl_2$]Cl_2		"		1609s	1687m	1198s	"	1588	-	440w
[Cu(SB) $TiCl_2$]Cl_2		"		1614s	1687m	1198s	"	1590	-	430w
[Cu(SB) $ZrCl_2$]Cl_2		"		1616s	1687m	1198s	"	1585	-	440w
[Cu(SB) $Sn(CH_3)_2$]Cl_2		"		1616s	1687m	1198s	"	1585	510w	
[Cu(SB) $Sn(C_2H_5)_2$]Cl_2		"		1609s	1687m	1198s	"	1590	510w	440w

SB = $C_{19}H_{24}N_4O_4$

s = sharp b = broad m = medium

Table 9 contd.

Complex	ν NH	νNO_2	ν C-S	ν C-C	ν NH	ν M-N	ν MCl
$C_4H_7NS_2O_2$ (L2)	-	1550	760S				
$[Cu(L^*_2)SiCl_2]Cl_2$	3100b 3185b	1550m	-	1150w 1440m	1578m	442w	330
$[Cu(L^*_2)GeCl_2]Cl_2$	3100b 3185b	1550m	-	1150w 1440m	1578m	516w	320
$[Cu(L^*_2)SnCl_2]Cl_2$	3100b 3185b	1550m	-	1150w 1440m	1578m	440w	320
$[Cu(L^*_2)TiCl_2]Cl_2$	3100b 3185b	1550m	-	1150w	1578m	440w	320
$[Cu(L^*_2)ZrCl_2]Cl_2$	3100b 3185b	1550m	-	1150w 1440m	1578m	435w	335
$[Cu(L^*_2)Sn(CH_3)_2]Cl_2$	3100b 3185b	1550m	-	1150w 1440m	1578m	435w	-
$[Cu(L^*_2)Sn(C_2H_5)_2]Cl_2$	3100b 3185b	1550m	-	1150w 1440m	1578m	440w	-

Table 10: Precent Inhibition data (a) A.niger (b) A. flavus (c) A. pori. percent mortality and LD_{50} cockroaches (d) with corresponding concentration of heterobimetallic complexes

Complex	Concentration	% inhibition	Log concentration in ppmx100	% Mortality	Probit value	LD_{50}
(a) $L_1/[Cu(SB)SnCl_2]^{++}$	2.00	60/65				
	2.50	65/70				
	3.00	70/80				
(b) $L_1/Cu(SB)SnCl_2]^{++}$	2.00	65/70				
	2.50	68/75				
	3.00	75/85				
(c) $L_1/Cu(SB)SnCl_2]^{++}$	2.00	59/64				
	2.50	64/69				
	3.00	68/75				
(d) $L_1 1/Cu(SB)SnCl_2]^{++}/$ $[Cu(SB)Sn(CH_3)_2]^{++}$			2.90	30/30/40	4.4756/4.4756/4.7467	10.96/
			2.95	30/40/50	4.4756/4.7467/5.0000	10.00/
			3.00	40/50/60	4.7467/5.0000/5.2533	8.91
			3.04	50/60/70	5.0000/5.2533/5.5244	
			3.07	60/70/80	5.0000/5.5244/5.8416	

CHAPTER V

NOVEL HETEROBIMETTALIC CHELATES OF N_2S_2 MACROCYCLIC LIGANDS (SS'-DIETHYL 1,3-DIAMINOPROPANE-DITHIOCARBAMATE) , (SS' CYCLOHEXYL-SPIRO (1,3 DIAMINOPROPANE-DITHIOCARBAMATE)

CHAPTER V

NOVEL HETEROBIMETALLIC CHELATESOF of N_2S_2 MACROCYCLIC LIGANDS [S,S DIETHYL-(1,3-DIAMINOPROPANE DITHIOCARBAMATE)] AND [S,S' CYCLOHEXYL-SPIRO (1,3-DIAMINOPROPANE DITHIOCARBAMATE)]

EXPERIMENTAL

Materials and Methods

Hydrated Mn(II), Co(II), Ni(II) and Cu(II) chloride, Fe(II) sulphate, carbondisulphide and cyclohexanone (BDH), 1,3-diaminopropane, dibromoethane (E.Merck) Ge(IV), (Sn(IV), Ti(IV), Zr(IV) tetrachloride and bis trimethylsilyl)amine (Fluka) were used as received.

Synthesis of [SS'diethyl(1,3-diaminopropane-dithiocarbamate)]L_1

CS_2 (0.02 mol, 1.20 mL) was dropwise added with constant stirring to 1,3-diaminopropane (0.01 mol, 0.84 mL) in ethanol (30 mL) followed by the addition of NaOH (0.80 g) dissolved in minimum quantity of H_2O at -15^oC. The resulting mixture was left for 3 h when a dark yellow solid precipitated. It was further refluxed with dibromoethane in methanol under reflux for ca. 24h. On standing this mixture overnight in refrigerator, a yellow product was separated. It was washed with ether and dried in vacuo.

Synthesis of [SS' cyclohexyl-spiro (1,3-diaminopropane-dithiocarbamate)]L_2

CS_2 (0.02 mol, 1.20 mL) was dropwise added with constant stirring to 1,3-diaminopropane (0.01 mol, 0.84 mL) in absolute ethanol (30 mL) at - 15^oC yielding off-white product on standing for 3h. It was thoroughly washed with ether and refluxed with cyclohexanone (0.01 mol, 1.32 mL) in 250 mL benzene for ca. 20 h. Benzene was removed through suction when it yielded fawn coloured crystalline product. It was thoroughly washed with ether and recrystallised from MeOH.

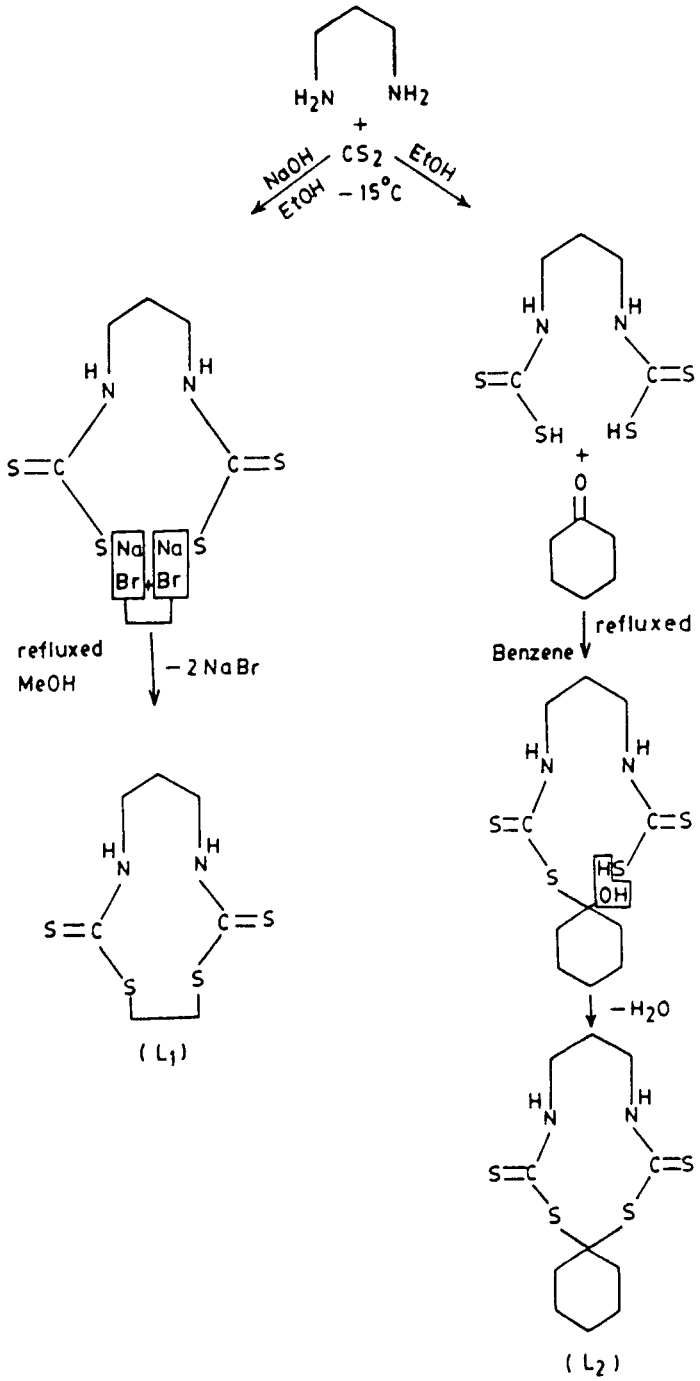
Synthesis of $[CuL_1]Cl_2$ complex

Hydrated $CuCl_2$(0.001 mol, 0.171g) was mixed with L_1 (0.001 mol, 0.252 g) in methanol (20 mL) with stirring and cooled to -10^oC when a white crystalline solid separated out. The crystals were separated and dried in vacuo. The same procedure was followed for the synthesis of Mn(II), Fe(II), Co(II) and Ni(II) complexes also.

Synthesis of $[CuL_2]Cl_2$ complex

To the solution of L_2 (0.001 mol, 0.306 g) in methanol (20 mL) was added $CuCl_2$ (0.001 mol, 0.171g) in a 100 mL flask in 1:1 ratio and left for about 2 h when a golden yellow compound separated out. It was washed with ether and dried in

SCHEME I


H2N NH2
+
CS2
NaOH EtOH
EtOH −15°C
refluxed
MeOH
−2 NaBr
(L1)
refluxed
Benzene
−H2O
(L2)

vacuo. The above procedure was followed for other complexes too. (Scheme II).

Synthesis of Group IV metal complexes

To the solution of L_1 (0.001 mol, 0.252g) or L_2 (0.001 mol, 3.01 g) in dry methanol (20 mL) was added anhydrous Group IV metal tetrachloride (0.001 mol) in 1:1 ratio. The mixture was thoroughly stirred and cooled to $-10^{o}C$ when coloured crystalline compounds separated out. They were washed with ether and dried in vacuo. (Scheme III).

Synthesis of heterobimetallic complexes of L_1 and L_2

The complexes $[ML_1]$ and $[ML_2]$ where $M=Cu^{2+}$, Ni^{2+}, Co^{2+} Fe^{2+}, Mn^{2+}, Ge(IV), Sn(IV), Ti(IV) and Zr(IV) tetrachlorides (0.001 mol) were treated with bis(trimethylsilyl)amine (0.002 mol) in dry DMF (20 ml) in 1:2 ratio at room temperature. Crystalline solids were separated on cooling the reaction mixture for about 2 h. They were washed with ether and dried in vacuo.

RESULTS AND DISCUSSION

The condensation of (1,3-diaminopropane)dithiocarbamate with cyclohexanone or dibromoethane yield 10 and 11 membered N_2S_2 macrocycles, respectively (Scheme 1) which are similar to those reported for a number of tetraimines.[103] They are stable to heat, oxidation by air and soluble in DMSO. The reaction of transition metal chlorides or Group IV metal tetrachlorides with the macrocycles is given in Scheme II and III.

It is evident that the ligand L_1 and L_2 react with MCl_4 by substitution of NH protons by metal and subsequent removal of two moles of HCl. The metal gets coordinated through two nitrogens and two sulphur atoms resulting in the formation of complexes. The low molar conductances (22-25 ohm^{-1} cm^2 mol^{-1}) of group IV tetrachloride complexes in anhydrous DMF show their non-electrolytic nature while the transition metal complexes are 1.2 electrolytes in DMSO (Table 11).

^1H NMR spectra

[SS' diethyl(1,3-diaminopropane) dithiocarbamate] L_1

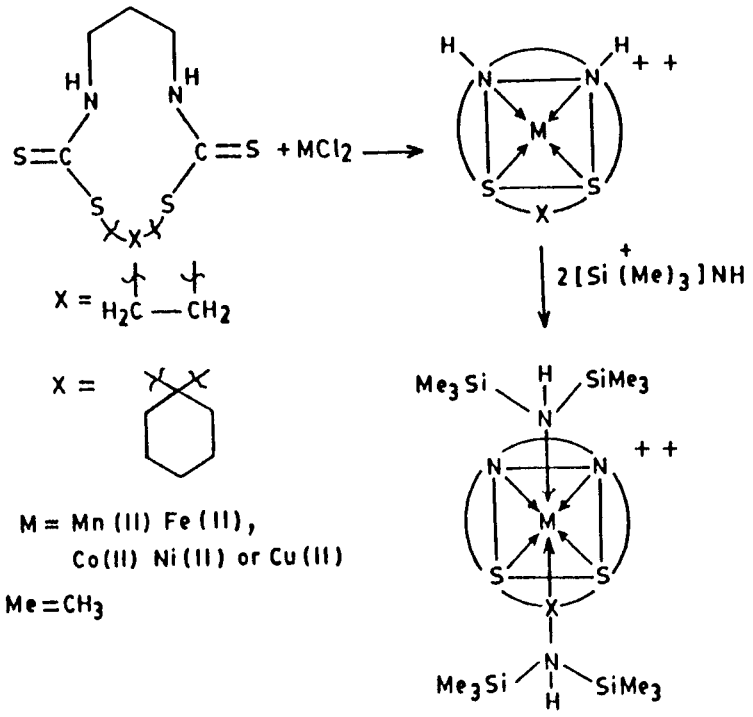
1.63 - 1.84 (2H, m, ß protons, $-C-CH_2-C-$)

3.02 - 3.05 (4H, m, $N-CH_2$ $-x-CH_2$ $-N$), J = 3Htz

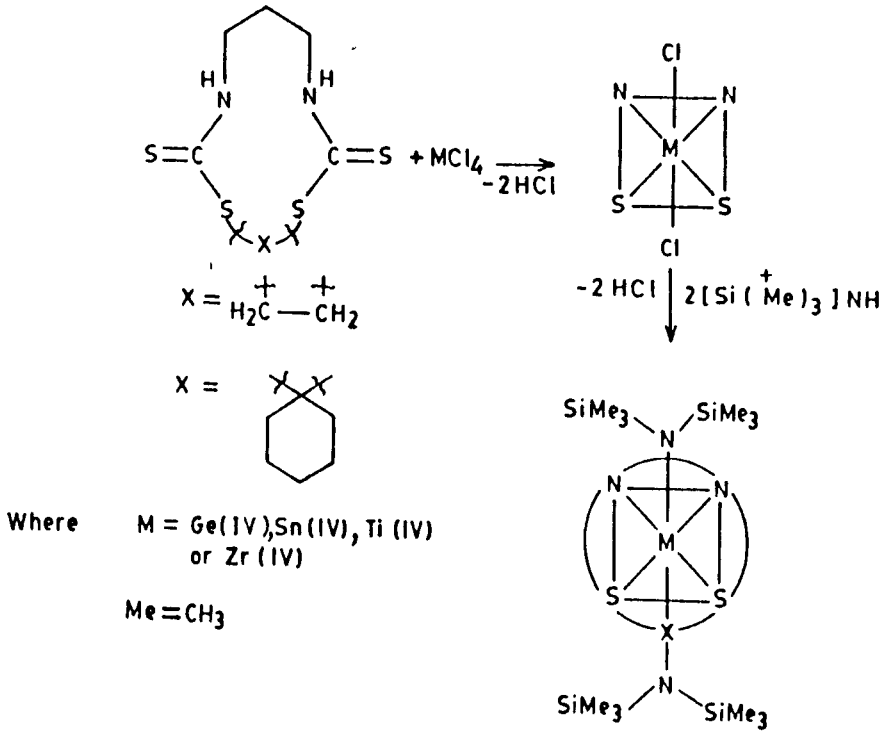
2.84 (4H, s-$S-CH_2$ - CH_2-S-)

7.77 (2H, s, NH NH)

SCHEME II



SCHEME III



[SS' cyclohexyl spiro(1,3-diaminopropane)dithiocarbamate]L_2

1.82(2H, m, ß protons, -C-CH_2-C- + 6H, m, ß cyclohexyl protons)

2.81-2.85 (8H, m,-CH_2-x-CH_2- + Cyclohexyl protons)

7.84 (2H, s, -NH NH).

IR spectra

Since the ligands do not show ν (S-H) at ca 2570 cm^{-1} their tautomerisation is ruled out. However, the presence of N-H band at 3250 cm^{-1} indicated that they exist only in thione form. It is further confirmed by NMR spectrum which does not show any signal at around 4 ppm due to absence of S-H proton. Since one of the two sulphur atoms of the dithiocarbamate group (Scheme I) is cyclised with 1,3-dibromoethane or cyclohexanone it is quite difficult to assign the CS_2 vibrations. According to the criterion of Bonati and Ugo[104], and Brinkhoff and Grotens[105] a symmetrically chelated dithiocarbamate may exhibit only one peak at about 1000 cm^{-1} while for an unsymmetrically bound dithiocarbamate moiety, this band splits into two closely spaced bands in 1000 $\pm$ 70 cm^{-1} range . However, we observed only one band in 1067-1092 cm^{-1} region and another band in 769-772 cm^{-1} region assigned to ν (C=S) and ν (C-S) respectively. The (C-S) stretching frequency shifts in all the complexes (740 cm^{-1} - 730 cm^{-1}) clearly indicated that one sulphur atom from each dithiocarbamate group is involved

in coordination. It is also obvious that the metal in the centre does not have the opportunity to bind with both the sulphur atoms. Also the ν (C=S) did not show any significant change to account for symmetrical coordination of CS_2 group.

Since the coordination of the metal ions occurs through N_2S_2 group of the macrocycles, the spectra of the transition metal complexes showed a large negative shift in ν NH (about 80 cm^{-1}) suggesting the binding of the amino group while a broad band at 3250 cm^{-1} ascribed to ν NH disappears in the complexes of Group IV metal ions indicating the removal of hydrogen atom from the N-H group. Other bands of medium intensity in 1300-1400 cm^{-1} ν [(C-C) and ν(C-N)], 1560-1580 cm^{-1} (δ NH) region have also been assigned.

The M-S and M-N stretching frequencies observed in 330-370 cm^{-1} and 420-550 cm^{-1} range further supported the coordination of sulphur and nitrogen atoms. The transition metal atom thus acquires square planar geometry. Transition metal ions have the tendency to expand their coordination number if an electron donating atom or group of atoms is available. When the compound $[M(L)]Cl_2$ is treated with bis(trimethylsilyl) amine, the lone pair of electrons on it is made available to the transition metal ion which coordinates through them and expands its coordination number

to six which is reflected from the additional Si-C (650 cm^{-1}), and, Si-N (440 cm^{-1}) stretching frequencies.[106]

Electronic Spectra

The absorption bands observed in the range 34364 cm^{-1} to 37453 cm^{-1} in all the complexes are attributed to the intraligand transitions. The weak bands observed at 17240 and 16129 cm^{-1} assigned to $^2B_{2g} \longleftarrow {}^2B_{1g}$ and $^2A_{1g} \longleftarrow {}^2B_{1g}$ transitions are characteristic of square planar geometry for Cu(II) ion. $[CuL(bis(trimethylsilyl)amine)_2]^{++}$ shows only one absorption band at 12987 cm^{-1} corresponding to $^2T_{2g} \text{---} {}^2E_g$ transition indicating a distorted octahedral geometry. Nickel(II) complexes show a broad band at 18691 cm^{-1} in the visible region which is typical of square planar geometry. It is lost in its complexes with bis(trimethylsilyl)amine due to a change in geoemtry from square planar to octahedral and new bands appear at 29300, 17500, 10050 cm^{-1} corresponding to the transitions $^3A_2(F) \text{----} \rangle {}^3T_1(P)$ $^3A_2(F) \text{-----} \rangle {}^3T_1(F)$ and $^3A_2(F) \text{-------} \rangle {}^3T_2(F)$ respectively, which are characteristic of octahedral nickel(II) ion.

The weak bands at 25,641 and 18,868 cm^{-1} ($^4A_{1g}(G) \text{--------} \rangle {}^6A_{1g}$ and $T_{1g}(G) \text{-----} \rangle A_{1g}$) in the case of manganese(II) complex also supports an octahedral geometry.

EPR Spectra

While EPR spectrum of $[(L_1\ Cu)\ Cl_2]$ shows $g_{\perp}$ (2.02) and g_{II} (2.17) corresponding to a distorted square planar geometry its complex with bis(trimethylsilyl)amine has values ($g_{\perp}$=2.56, g_{II}=2.057) fitting in a distorted octahedral array.

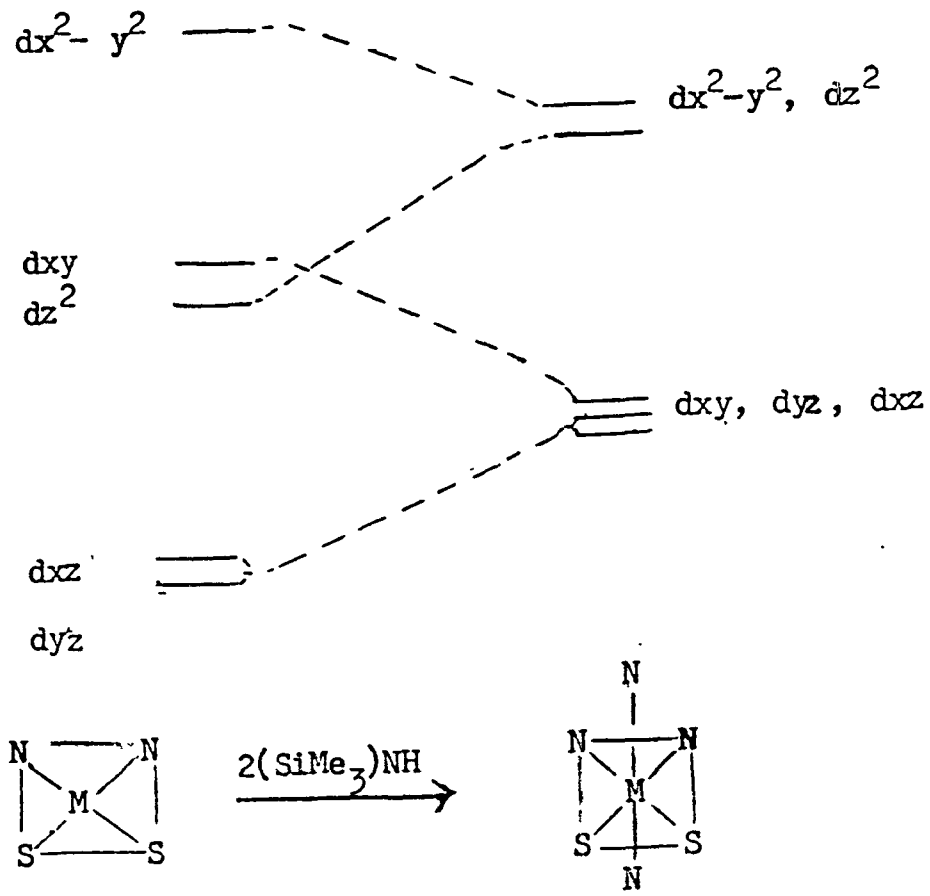


Table 11: Analytical data, colour, melting points and % yield of the ligands L_1,L_2 and their complexes

Complexes	Colour	M.P. °C	Yield %	% Calcd. (Found)					$ohm^{-1}cm^2 mol^{-1}$
				C	H	N	S	Cl	
$C_7H_{12}N_2S_4$ (L_1)	Light Yellow	195	70	33.33 (33.54)	4.76 (4.78)	11.11 (11.12)	50.79 (51.00)		
$[Mn(L_1)Cl_2$	Cream	223	35	22.19 (22.29)	3.17 (3.19)	7.39 (7.40)	33.82 (33.98)	18.76 (18.81)	78
$[Fe(L_1)]SO_4$	Cream	218	38	20.84 (20.96)	2.97 (2.99)	6.94 (6.96)	39.70 (30.74)	-	73
$[Co(L_1)]Cl_2$	Brown	220	35	21.96 (22.09)	3.13 (3.14)	7.32 (7.33)	33.47 (33.62)	18.56 (18.58)	72
$[Ni(L_1)]Cl_2$	Cream	234	38	21.98 (22.13)	3.14 (3.16)	7.32 (7.34)	33.49 (33.68)	18.58 (18.65)	78
$[Cu(L_1)Cl_2$	Light Yellow	270	45	21.73 (21.85)	3.10 (3.12)	7.24 (7.25)	33.11 (33.23)	18.36 (18.39)	73
$[MnL_1(Si_2Me_6NH)_2]Cl_2$	Cream	218	43	32.18 (32.29)	7.05 (7.09)	7.90 (7.92)	18.06 (18.16)	10.02 (10.12)	79
$[FeL_1(Si_2Me_6NH)_2]SO_4$	Yellow	227	45	31.53 (31.62)	6.91 (6.93)	7.24 (7.27)	22.13 (22.23)	-	74
$[CoL_1(Si_2Me_6NH)_2]Cl_2$	Brown	223	42	32.39 (32.43)	7.10 (7.12)	7.95 (7.99)	18.18 (18.25)	10.08 (10.14)	73
$[NiL_1(Si_2Me_6NH)_2]Cl_2$	Cream	212	40	32.43 (32.51)	7.11 (7.13)	7.96 (7.99)	18.20 (18.31)	10.09 (10.13)	78
$[CuL_1(Si_2Me_6NH)_2]Cl_2$	Yellow	243	40	32.18 (32.27)	7.05 (7.08)	7.90 (7.94)	18.06 (18.19)	10.02 (10.10)	71

Table 11 contd.

Complexes	Colour	M.P. °C	Yield %	% Calcd. (Found)					$ohm^{-1} cm^2 mol^{-1}$
				C	H	N	S	Cl	
$C_{11}H_{18}N_2S_4$ (L_2)	Light brown	218	57	43.13 (44.10)	5.88 (5.98)	9.15 (9.28)	41.83 (43.53)	-	-
$[Mn(L_2)]Cl_2$	Cream	198	40	30.52 (31.82)	4.16 (4.29)	6.46 (6.59)	29.60 (30.63)	16.53 (16.98)	79
$[Fe(L_2)]SO_4$	Light yellow	196	43	28.83 (29.16)	3.90 (4.10)	6.11 (6.20)	34.94 (35.99)	-	78
$[Co(L_2)]Cl_2$	Light brown	193	42	30.24 (30.64)	4.12 (4.23)	6.41 (6.46)	29.33 (29.93)	16.38 (16.43)	77
$[Ni(L_2)]Cl_2$	Cream	198	40	30.26 (28.45)	4.12 (4.27)	6.42 (6.62)	20.35 (29.65)	16.39 (16.43)	78
$[Cu(L_2)]Cl_2$	Golden yellow	198	50	29.93 (28.16)	4.08 (4.20)	6.34 (6.40)	29.03 (29.23)	16.19 (16.39)	72
$[MnL_2(Si_2Me_6NH)_2]Cl_2$	Cream	203	38	36.41 (36.61)	7.12 (7.22)	7.38 (7.44)	16.88 (17.07)	9.43 (9.53)	78
$[FeL_2(Si_2Me_6NH)_2]SO_4$	Yellow	192	40	35.48 (35.53)	6.94 (6.98)	7.19 (7.29)	20.57 (20.77)	-	74
$[CoL_2(Si_2Me_6NH)_2]Cl_2$	Brown	187	38	35.48 (35.68)	7.12 (7.23)	7.38 (7.46)	16.88 (17.10)	9.43 (9.54)	73
$[NiL_2(Si_2Me_6NH)_2]Cl_2$	Cream	183	42	36.43 (36.51)	7.12 (7.52)	7.39 (7.49)	16.89 (17.10)	9.43 (9.55)	53
$[CuL_2(Si_2Me_6NH)_2]Cl_2$	Yellow	194	45	36.22 (36.44)	7.08 (7.18)	7.34 (7.46)	16.79 (16.99)	9.38 (9.49)	63

Si_2Me_6NH = bis(trimethylsilyl)amine

Table 12: Important IR spectral data for the ligands L_1,L_2 and their complexes

Complexes	ν NH cm^{-1}	ν C-N cm^{-1}	ν C-S cm^{-1}	ν C=S cm^{-1}	δNH cm^{-1}	ν M-S cm^{-1}	ν M-N cm^{-1}
$C_7H_{12}N_2S_4$ (L_1)	3250	1380s	769s	1067s	1560m	-	
$[Mn(L_1)]Cl_2$	3180b	1370s	740s	1068s	1565m	340	460
$[Fe(L_1)]SO_4$	3175b	1368s	743s	1067s	1560m	335	463
$[Co(L_1)]Cl_2$	3178b	1371s	741s	1070s	1563m	360	465
$[Ni(L_1)]Cl_2$	3181b	1365s	740s	1068s	1563m	355	463
$[Cu(L_1)]Cl_2$	3180b	1370s	735b	1068s	1565m	355	470
$[MnL_1(Si_2Me_6NH)_2]Cl_2$	3180b	1375s	730s	1067s	1560m	340	460
$[FeL_1(Si_2Me_6NH)_2]Cl_2$	3178b	1371s	734s	1067s	1563m	334	463
$[CoL_1(Si_2Me_6NH)_2]Cl_2$	3179b	1381s	731s	1068s	1565m	363	464
$[NiL_1(Si_2Me_6NH)_2]Cl_2$	3180b	1378s	730s	1088s	1560m	355	470
$[CuL_1(Si_2Me_6NH)_2]Cl_2$	3175b	1379s	730s	1088s	1560m	355	470

Table 12 contd.

Complexes	ν NH cm^{-1}	ν C-N cm^{-1}	ν C-S cm^{-1}	ν C=S cm^{-1}	δNH cm^{-1}	ν M-S cm^{-1}	ν M-N cm^{-1}
$C_{11}H_{18}N_2$ (L_2)	3250b	1390s	772s	1092s	1580m	-	-
$[Mn(L_2)]Cl_2$	3180b	1368s	743s	1067s	1565m	335	465
$[Fe(L_2)]CO_4$	3178b	1368s	743s	1067s	1560m	340	463
$[Co(L_2)]Cl_2$	3175b	1370s	740s	1073s	1563m	355	470
$[Ni(L_2)]Cl_2$	3180b	1368s	743s	1068s	1563m	334	470
$[Cu(L_2)]CO_2$	3178b	1378s	738s	1092s	1580m	338	464
$[Mn.L_2(Si_2Me_6NH)_2]Cl_2$	3180b	1376s	736s	1067s	1560m	363	460
$[Fe.L_2(Si_2Me_6NH)_2]SO_4$	3175b	1370s	738s	1067s	1563m	355	460
$[Co.L_2(Si_2Me_6NH)_2]Cl_2$	3180b	1380s	734s	1068s	1565m	355	464
$[Ni.L_2(Si_2Me_6NH)_2]Cl_2$	3178b	1378s	735s	1091s	1578m	338	470

Table 13 : Analytical data of the ligands, L_1,L_2 and their complexes

Complexes	M.P. °C	Colour	Yield %	% Calcd. (Found)				
				C	H	N	S	Cl
[L_1 $GeCl_2$]	238	Cream	58	21.87 (22.02)	2.60 (2.63)	7.29 (7.33)	33.33 (33.67)	18.61 (18.82)
[L_1 $SnCl_2$]	225	Yellow	60	19.11 (19.23)	2.27 (2.39)	6.37 (6.49)	29.10 (29.45)	16.26 (16.86)
[L_1 $TiCl_2$]	228	Orange	53	22.74 (22.96)	2.70 (2.81)	7.58 (7.69)	34.66 (34.99)	17.30 (17.50)
[L_1 $ZrCl_2$]	228	Orange	48	20.35 (20.48)	2.42 (2.53)	6.78 (6.87)	31.01 (31.33)	19.36 (19.50)
[L_1 $Ge(Si_2Me_6N)_2$]	185	Yellow	58	35.46 (35.69)	7.15 (7.26)	8.71 (8.83)	19.91 (20.23)	
[L_1 $Sn(Si_2Me_6N)_2$]	180	Brown	62	33.13 (33.34)	6.68 (6.79)	8.13 (8.24)	18.60 (18.73)	
[L_1 $Ti(Si_2Me_6N)_2$]]	183	Orange	63	36.90 (34.23)	7.44 (7.56)	9.06 (9.15)	20.71 (20.98)	
[L_1 $Zr(Si_2Me_6N)_2$]	178	Orange	65	34.48 (34.68)	6.95 (7.68)	8.46 (9.57)	19.35 (19.56)	

Table 13 contd.

Complexes	M.P. °C	Colour	Yield %	% Calcd. (Found)				
				C	H	N	S	Cl
$[L_2 Ge Cl_2]$	230	Brown	57	29.46 (29.78)	3.66 (3.78)	6.25 (6.36)	28.57 (28.87)	15.95 (16.00)
$[L_2 Sn Cl_2]$	233	Yellow	63	26.74 (26.98)	3.24 (3.33)	5.69 (5.71)	25.93 (26.03)	
$[L_2 Ti Cl_2]$	236	Orange	68	31.20 (31.39)	3.71 (3.82)	6.61 (6.73)	25.93 30.23	16.77 (16.98)
$[L_2 Zr Cl_2]$	238	Orange	53	28.31 (28.44)	3.43 (3.54)	6.00 (6.12)	28.31 (28.56)	
$[L_2Ge(Si_2Me_6N)_2]$	195	Orange	58	39.65 (39.97)	7.47 (7.58)	8.04 (8.13)	18.39 (18.42)	
$[L_2Sn(Si_2Me_6N)_2]$	188	Oorange	62	37.19 (37.23)	7.00 (7.11)	7.54 (7.63)	17.25 (17.45)	
$[L_2Ti(Si_2Me_6N)_2]$	198	Orange	63	41.10 (41.43)	7.74 (7.85)	8.33 (8.44)	19.06 (19.20)	
$[L_2Zr(Si_2Me_6N)_2$	193	Orange	59	38.59 (38.88)	7.27 (7.32)	7.82 (7.91)	17.89 (17.99)	

Table 14: Important IR absorption (cm^{-1}) of the ligand L_1,L_2 and their complexes

Complexes	νNH	ν C-S	ν C-N	ν C=S	ν M-S	ν M-N	ν M-Cl
$[L_1GeCl_2]$	-	730	1320	1066	340	545	346
$[L_1SnCl_2]$	-	746	1310	1067	370	425	280
$[L_1TiCl_2]$	-	735	1320	1065	360	540	330
$[L_1ZrCl_2]$	-	738	1320	1066	365	550	320
$[L_2GeCl_2]$	-	735	1320	1090	370	540	342
$[L_2SnCl_2]$	-	738	1320	1092	370	425	330
$[L_2Ti_2]$	-	740	1320	1067	365	630	320
$[L_2Zr_2]$	-	740	1320	1067	368	425	320
$[L_1Ge(Si_2Me_6N)_2]$	-	740	1310	1067	368	530	-
$[L_1Sn(Si_2Me_6N)_2]$	-	738	1320	1092	365	425	-
$[L_1Ti(Si_2Me_6N)_2]$	-	736	1320	1092	365	425	-
$[L_1Zr(Si_2Me_6N)_2]$	-	735	1320	1092	370	425	-
$[L_2Ge(Si_2Me_6N)_2]$	-	735	1320	1092	370	425	-
$[L_2Sn(Si_2Me_6N)_2]$	-	735	1320	1092	370	425	-
$[L_2Ti(Si_2Me_6N)_2]$	-	735	1320	1092	370	425	-
$[L_2Zr(Si_2Me_6N)_2]$	-	735	1320	1092	370	425	-

CHAPTER VI

SYNTHESIS, CHARACTERIZATION AND TOXICITY OF HETEROBIMETALLIC CHELATES OF POLYDENTATE NITROGEN CONTAINING LIGANDS

CHAPTER VI

SYNTHESIS, CHARACTERISATION AND TOXICITY OF HETEROBIMETALLIC CHELATES OF POLYDENTATE NITROGEN CONTAINING LIGANDS

EXPERIMENTAL

Materials and methods

N,N,N',N'-ethylene diamine tetra acetic acid, mercapto acetic acid, thiodiglycolic acid and o-phenylenediamine (E.Merck), hydrated Co(II), Ni(II), Cu(II) and Zn(II) nitrates (B.D.H.), Si(IV), Ge(IV), Sn(IV), Ti(V), and Zr(IV) tetrachlorides, diethyl - and dimethyltindichlorides (Fluka) were used without further purification. Ethanol and methanol (B.D.H.) were used as received.

Physical Measurements

Microanalyses were performed on a Perkin Elmer 240-B microanalyser. IR and for IR spectra were recorded on a Perkin Elmer 240 FT spectrophotometer as KBr discs and on a Perkin Elmer 621 spectrophotometer in nujol respectively. The UV-visible and EPR spectra were recorded on a Pye Unicam PU 8800 spectrophotometer and Bruker ESP-300-X-band spectrometer respectively. The conductivity measurements were done on an Elico conductivity bridge type CM-82T. Magnetic susceptibility measurements were done with a vibration sample magnetometer model 155 at room temperature.

Synthesis of N,N,N',N'-tetrakis (2-benzimidazolyl) methyl 1-2 ethanediamine [TBED] [107]

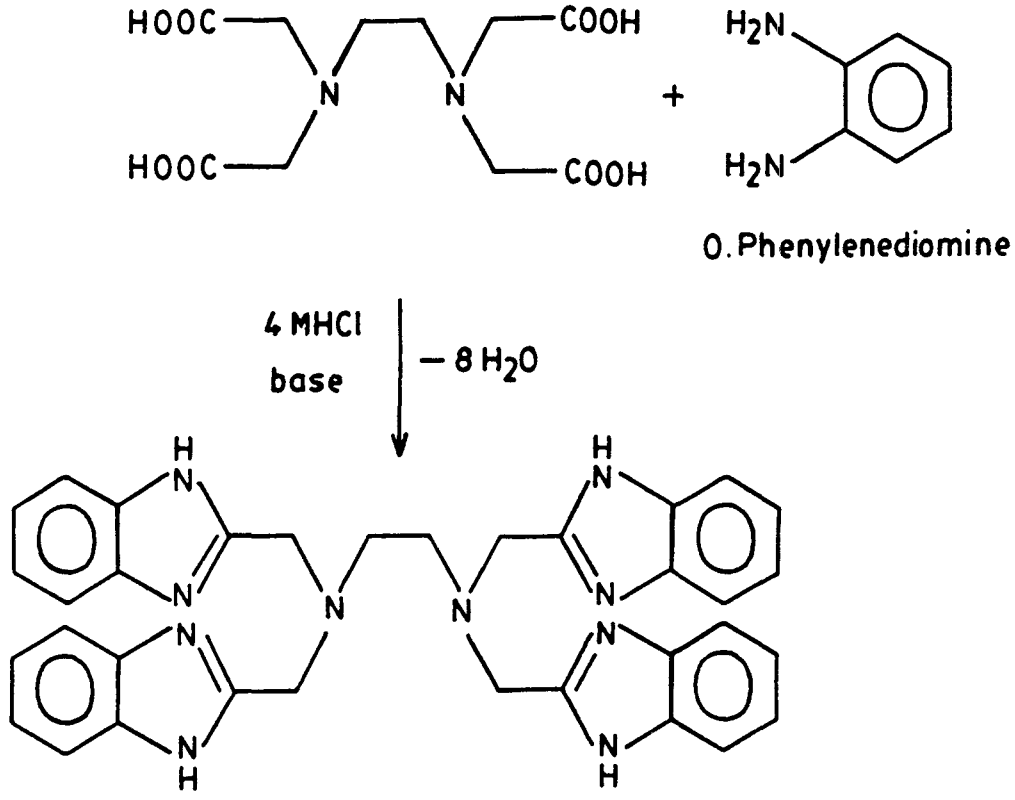
EDTA [0.033 mol, 9.64 g] and o-phenylenediamine (0.2 mol, 21.69 g) were ground and thoroughly mixed together followed by heating of the mixture in a paraffin oil bath at 180-190°C. After stirring for 60 minutes when the effervescence ceased to evolve, the mixture was cooled and 150 mL of 4M HCl was added. The bluish precipitate obtained after several h of standing was filtered out, washed by slurrying in acetone, and dried in air as hydrochloride of TBED. The salt was dissolved in hot water and neutralized by concentrated ammonia - water mixture in 1:9 ratio. The wet precipitate obtained by filtration was recrystallised from acetone to give off-white solid.

Anal. Cacl. (Found) for $C_{34}H_{32}N_{10}.C_3H_6O$: yield 58%M.P. 174°C , %C, 69.57 (71.31); %H, 6.00 (6.29); %N, 21.93 (21.73).

Synthesis of bis (thio methyl benzimidazole) [BTMB] [108]

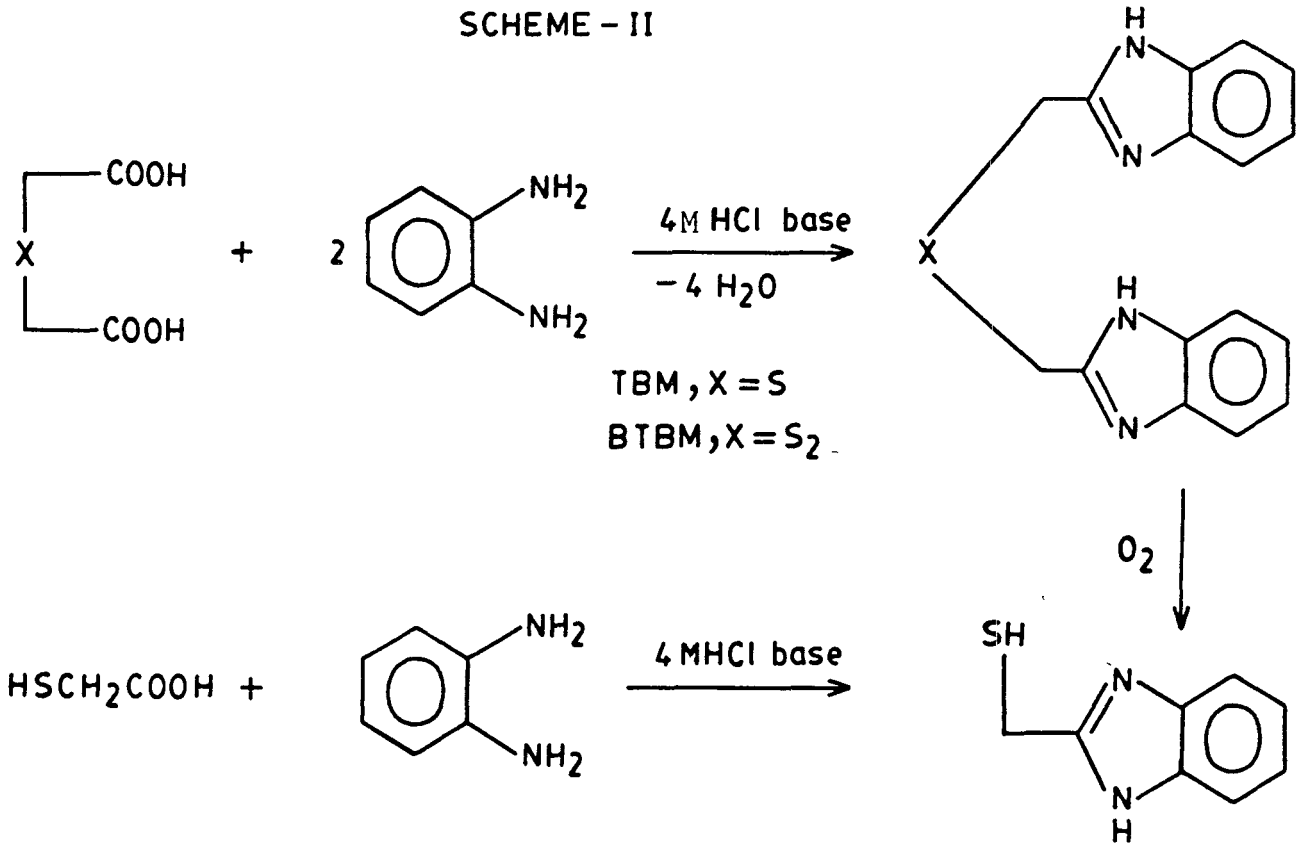
A mixture of Mercapto acetic acid (0.1 mol) and o-phenylene diamine (0.1 mol) in 150 mL of 4M HCl was refluxed in a flask for 24 h. The contents were then cooled to room temperature and neutralised with 4M ammonia.which afforded a precipitate. It was filtered, redissolved in MeOH and air oxidised which yielded the desired compound.

SCHEME - I



(TBED)

SCHEME - II


COOH
X
COOH
+
2
NH2
NH2
4M HCl base
−4 H2O
TBM, X = S
BTBM, X = S2
H
N
N
X
H
N
N
O2
HSCH2COOH +
NH2
NH2
4 MHCl base
SH
N
N
H

This precipitate was separated by suction and crystallised from EtOH.

Anal: Cacl. (Found) for C_{16} H_{14} N_4 S_2, M.P. 183 % C 58.89 (59.20); %H, 4.29 (4.38), %N 17.17 (17.37).

^{1}H NMR (CD_3OD) 12.64 (2H S) 7.7 (4H, m), 7.15 (4H. m) 4.0 (4H, S)

Synthesis of thio bis (methyl benzimidazole)[TMB]

Thiodiglycolic acid (0.10 mol) was combined with 0.20 mol o-phenylene diamine in 150 mL of 4M HCl. The mixture was refluxed for 24h and neutralized with 4N NH_4OH which yielded a white paste like precipitate. It was washed with ether and dried in vacuo.

Anal. Cacl. (Found)for ($C_{16}H_{14}N_4S$):Yield 60%, M.P. 184^{o}C(d), : %C, 64.30 (64.36) %H, 4.89 (5.30) %N, 18.75 (18.90)

^{1}H NMR; $(CD_3)_2$ SO, : 7.6 (4H, m) 7.2 (4H, m), 4.05 (4H, S)

Synthesis of complexes of TBED / TMB with transition metals

Hydrated M $(NO3)_2$ (0.2mmol) was added to a solution of TBED (0.2mmol) in 30 mL of hot absolute ethanol or (0.4 mmol) of TMB in 30 mL of hot acetonitrile. The mixture was refluxed for 6 h and left overnight when crystalline compounds were obtained. They were washed with ethanol, diethyl ether and dried in vacuo.

Synthesis of heterobimetallic complexes

MCl_4 or R_2SnCl_2 (0.1 mmol) was added to $[M(TBED)](NO_3)_2$ or $[M(TMB)_2]$ $(NO3)_2$ (0.1mmol) in 20 mL dry DMF and was refluxed for 4 h. On cooling the mixture to room temperature, crystalline solids separated out which were filtered, washed with ether and dried in vacuo. It could not be recrystallised from DMF since the slurry becomes sticky.

Synthesis of heterobimetallic complexes of [BTMB]

BTMB (0.2 mmol) in 20 mL absolute EtOH was mixed with $M(NO_3)_2$ (0.1 mmol) (M=divalent transition metal ion) which did not show any change except when Group IV tetrachlorides or diethyltin dichloride and dimethyltindichloride (0.1 mmol) was added to this mixture at room temperature. An amorphous solid precipitated which was filtered, washed with ether and dried in vacuum. All these manipulations were done in a closed system to prevent access of air and moisture.

Toxicity

Five sets of experiments were done. The insects (cockroaches) were fed on the compounds in varying concentration ranging from 5-9 ppm. Standard method of evaluation was adopted. Fungitoxicity was also evaluated by agar plate method.

RESULTS AND DISCUSSION

Analytical data (Table 15) and molar conductances conform to the composition, $[M(TBED*)M'Cl_2](NO_3)_2$, $[M(BTMB*)_2M'\ Cl_2](NO3)_2$, $[M(TMB*)_2\ M'Cl_2]\ (NO_3)_2$

The synthesis may be represented according to the scheme.

$$TBED + M(NO3)_2 \longrightarrow [M(TBED)]\ (NO3)_2$$

$$[M(TBED)](NO3)_2 + M\ Cl_4/R_2\ SnCl_2 \longrightarrow [M(TBED^{*})'MCl_2](NO3)_2 + 2HCl$$

$$2TMB + M(NO3)_2 + M\ Cl_4/\ R_2SnCl_2 \longrightarrow [M(TMB^{*})_2]M\ Cl_2](NO3)_2 + 2HCl$$

$$2BTMB + M(NO3)_2 + M'Cl_4/R_2SnCl_2 \longrightarrow [M(BTMB^{*})_2M'\ Cl_2](NO3)_2 + 2HCl$$

where M = Co(II), Ni(II), Cu(II), Zn(II), M' = Ge (IV), Sn(IV), Ti(IV) and Zr (IV) and R_2SnCl_2

* = deprotonated ligand

Metal ion is octahedrally coordinated while the Group IV metal atoms show tetrahedral geometry. The complexes are stable to air, ionic in nature and soluble in DMF and DMSO.

^1H NMR

Since the complex is formed by the replacement of proton the NH proton signal (12.64 - 13.00 ppm) in the free ligand disappears in the complexes.Other signals remain unaltered. The NMR spectrum of $[Zn(TBED)^*SnR_2](NO_3)_2$ is identical to $[Zn(TBED^*]SnCl_2](NO_3)_2$ except for CH_3 or C_2H_5 proton signal appearing in 1.30 - 4 ppm range.

IR spectra

The IR data for heterobimetallic complexes is given in (Table 16). The ν NH due to amino group in the free ligand at 3250 cm^{-1} is negatively shifted by about 30 cm^{-1} in the transition metal complexes as a consequence of the decrease in electron density at the nitrogen atom due to coordination. Since the complexes contain both bonded and free donor sites it is difficult to distinguish between bonded and nonbonded νC-N, νN-H in the complexes.[109] However, Two medium intensity bands observed at 1640 cm^{-1} and 1480 cm^{-1} have been assigned to ν C=N and ν C-N respectively, which were shifted to lower wave number after coordination. A comparison of the free ligand with those of the complexes reveals the appearance of additional bands in the range 280-520 assigned to ν M-N and ν M-Cl[110]. IR spectrum of BTMB/ TMB is nearly identical with that of the TBED except for the ν C-S which appears at 760 cm^{-1} - 730 cm^{-1} region.

The presence of νM-Cl or ν Sn-C (580 cm^{-1}) in the spectra of heterobimetallic complexes ascertains the insertion of a second metal.

Magnetic moment and electronic spectra

The absorption bands above 30000 cm^{-1} are due to charge transfer transitions (Table 17).

Magnetic moment (4.78 BM) in the case of Co^{2+} ion corresponds to a quartet state, S = 3/2. In an octahedral field, the ground state is orbitally triply degenerate and would cause an orbital angular momentum contribution to the magnetic mement. The moment, therefore, would lie between the limits of $[4s\ (S+1)]^{1/2}$ = 3.88 BM and $[4S(S=1) + L\ (L+1)^{1/2}]$ = 5.2 BM. The magnetic moment of the complexes is close to that expected for a octahedral metal ion in high spin state indicating a T_{1g} ground term with large orbital moment contribution. The electronic spectra of Co^{2+} complexes displays two sharp bands at 8700 cm^{-1} and 21000 - 22222 cm^{-1} in addition to a shoulder at 19267 cm^{-1} which have been assigned to $^4T_{2g}$ (F) <----- $^4T_{1g}$ (F), A_{2g} (F) <---- $^4T_{1g}$ (F) and $^4T_{1g}$ (P) <------ $^4T_{1g}$ (F) transitions respectively and support the above geometry for Co^{2+} ion[102].

The magnetic moment of Ni(II) ion (3.4 BM) is in accord with that normally accepted for octahedral Ni(II)

ion. The electronic spectral bands at 14705 cm^{-1} and 24390 cm^{-1} assigned to $^3T_{1g}$ (F) <--- $^3A_{2g}$(T) and $^3T_{1g}$ (P)<---$^3A_{2g}$(F) transition, also suggest an octahedral geometry for the metal ion.

The bimetallic complexes containing Cu(II) are paramagnetic with one unpaired electron (1.87 BM). The electronic spectral band at 12406 cm^{-1} assigned to T_{2g}<--^2Eg transition suggests that Cu(II) is in an octahedral environment which is also supported by EPR spectral data (g_{11} 2.30, $g_{\perp}$ 2.16), though a distortion from octahedral geometry must occur. The slight variation in magnetic moment may be due to diamagnetic effect on central metal ion.

Toxicity:

The efficacy of metal complexes of TBED, TMB or BTMB and their heterobimetallic complexes are given in (Table 18). It has been noted that compounds containing two metals cause a substantial enhancement in toxicity.

Table-15: Analytical data, M.P. yield and molar conductance of heterobimetallic complexes of TBED, BTMB, TMB with transition metals and group (IV) metal tetra chlorides.

Complex	M.P. (^{o}C)	Colour	% Yield	% Calcd. (Found)				ohm_2^{-1} $cm.^{2}$ $mol.^{-1}$
				C	H	N	Cl	
[Co (TBED*) Si Cl_2] $(NO_3)_2$	260d	Brown	64	47.44 (47.73)	3.48 (3.59)	19.53 (19.73)	8.25 (8.98)	133.00
[Co (TBED*) Ge Cl_2] $(NO_3)_2$	268d	Brown	63	45.10 (45.62)	3.31 (3.53)	18.57 (18.82)	7.84 (8.21)	130.20
[Co (TBED*) Sn Cl_2] $(NO_3)_2$	272d	Brown	64	42.95 (43.25)	3.15 (3.33)	17.59 (17.83)	7.47 (7.92)	136.62
[Co (TBED*) Ti Cl_2] $(NO_3)_2$	280d	Brown	60	46.37 (46.88)	3.40 (3.62)	19.09 (19.36)	8.06 (8.36)	130.00
[Co (TBED*) Zr Cl_2] $(NO_3)_2$	265d	Brown	60	44.19 (44.70)	3.29 (2.48)	18.19 (18.39)	7.69 (7.99)	136.00
[Co (TBED*) Sn $(CH_3)_2$] $(NO_3)_2$	275d	Brown	66	47.52 (47.93)	3.96 (4.12)	18.48 (18.73)	-	130.00
[Co (TBED*) Sn $(C_2H_5)_2$] $(NO_3)_2$	273d	Brown	65	48.66 (49.13)	4.26 (4.43)	17.79 (17.91)	-	130.00
[Ni (TBED*) Si Cl_2] $(NO_3)_2$	248d	Voilet	55	47.45 (47.82)	3.48 (3.65)	19.54 (19.72)	8.25 (2.88)	140.00
[Ni (TBED*) Ge Cl_2] $(NO_3)_2$	249d	Voilet	56	45.11 (45.63)	3.31 (3.56)	18.50 (18.75)	7.85 (8.15)	139.63
[Ni (TBED*) Sn Cl_2] $(NO_3)_2$	246d	Grey	58	42.96 (43.23)	3.15 (3.39)	17.68 (17.92)	7.47 (7.88)	138.60

Table 15 Contd.

Complex	M.P. (^{o}C)	Colour	% Yield	% Calc. (Found)				$ohm_{,}^{-1}$ $cm.^{2}$ $mol.^{-1}$
				C	H	N	Cl	
[Ni (TBED*) Ti Cl_2] $(NO_3)_2$	247d	Grey	57	46.38 (46.82)	3.41 (3.69)	18.64 (18.89)	8.07 (8.46)	140.92
[Ni (TBED*) Zr Cl_2] $(NO_3)_2$	250d	Grey	58	44.20 (44.68)	3.25 (3.52)	18.20 (18.33)	7.69 (7.93)	138.64
[Ni (TBED*) Sn $(CH_3)_2$] $(NO_3)_2$	255d	Grey	62	47.54 (47.93)	3.96 (4.13)	18.48 (18.69)	-	138.00
[Ni (TBED*) Sn $(C_2H_5)_2$] $(NO_3)_2$	258d	Grey	65	48.71 (48.96)	4.20 (4.38)	17.94 (18.10)	-	138.00
[Cu (TBED*) Si Cl_2] $(NO_3)_2$	255d	Green	56	47.19 (47.58)	3.46 (3.67)	19.43 (19.27)	8.21 (8.53)	133.00
[Cu (TBED*) Ge Cl_2] $(NO_3)_2$	253d	Brown	55	44.87 (45.23)	3.29 (3.39)	18.46) (18.68)	7.80 (8.21)	134.60
[Cu (TBED*) Sn Cl_2] $(NO_3)_2$	250d	Yellow	52	42.74 (43.13)	3.14 (3.26)	17.59 (17.69)	7.43 (7.94)	133.00
[Cu (TBED*) Ti Cl_2] $(NO_3)_2$	258d	Yellow	53	46.12 (46.54)	3.39 (3.51)	18.99 (19.13)	8.02 (8.62)	134.00
[Cu (TBED*) Zr Cl_2] $(NO_3)_2$	240d	Yellow	56	43.97 (44.30)	3.23 (3.43)	18.10 (18.23)	7.65 (7.93)	133.00
[Cu (TBED*) Sn $(CH_3)_2$] $(NO_3)_2$	249d	Yellow	56	47.32 (47.88)	3.92 (4.10)	18.38 (18.59)	-	-

Table 15 Contd.

Complex	M.P. (°C)	Colour	% Yield	% Calc. (Found) C	H	N	Cl	$ohm.^{-1} cm.^{2} mol.^{-1}$
[Cu (TBED*) Sn $(C_2H_5)_2$] $(NO_3)_2$	253d	Yellow	58	48.43 (48.82)	4.24 (4.36)	17.84 (17.93)	-	-
[Zn (TBED*) Si Cl_2] $(NO_3)_2$	250d	Brown	48	47.09 (47.48)	3.46 (3.62)	19.39 (19.46)	8.19 (8.87)	136.00
[Zn (TBED*) Ge Cl_2] $(NO_3)_2$	259d	Brown	43	44.78 (45.32)	3.29 (3.38)	18.44 (18.60)	7.79 (8.20)	-
[Zn (TBED*) Sn Cl_2] $(NO_3)_2$	258d	Brown	48	42.66 (43.38)	3.13 (3.28)	17.15 (17.28)	7.42 (7.98)	134.00
[Zn (TBED*) Ti Cl_2] $(NO_3)_2$	253d	Brown	47	46.03 (46.54)	3.38 (3.49)	18.95 (19.08)	8.01 (8.68)	136.00
[Zn (TBED*) Zr Cl_2] $(NO_3)_2$	257d	Brown	43	43.96 (44.36)	3.23 (3.36)	17.66 (17.78)	7.64 (7.93)	133.00
[Zn (TBED*) Sn $(CH_3)_2$] $(NO_3)_2$	258d	Brown	48	47.23 (47.75)	3.93 (4.12)	17.92 (18.13)	-	-
[Zn (TBED*) Sn $(C_2H_5)_2$] $(NO_3)_2$	259d	Brown	49	48.35 (48.86)	4.24 4.44)	17.80 (17.93)	-	-
[Cu (BTMB*) Si Cl_2] $(NO_3)_2$	240d	Yellow	58	41.00 (41.50)	2.77 (2.89)	14.94 (15.12)	7.58 (7.90)	136.0
[Cu (BTMB*) Ge Cl_2] $(NO_3)_2$	248d	Yellow	53	39.13 (39.68)	2.64 (2.78)	14.26 (14.39)	7.23 (7.78)	133.6

Table 15 Contd.

Complex	M.P. (^{o}C)	Colour	% Yield	% Calc. (Found)				$ohm^{-1} cm.^{2} mol.^{-1}$
				C	H	N	Cl	
[Cu (BTMB*) Sn Cl_2] $(NO_3)_2$	253d	Yellow	55	37.40 (37.88)	2.53 (2.64)	13.63 (13.78)	6.91 (7.32)	133.2
[Co (BTMB*) Si Cl_2] $(NO_3)_2$	260d	Pink	38	41.20 (41.63)	2.78 (2.86)	15.02 (15.14)	-	131.20
[Co (BTMB*) Ge Cl_2] $(NO_3)_2$	263d	Pink	37	39.32 (39.73)	2.66 (2.77)	14.33 (14.43)	-	-
[Co (BTMB*) Sn Cl_2] $(NO_3)_2$	255d	Pink	40	37.57 (37.90)	2.54 (2.66)	13.69 (13.73)	6.99 (7.13)	133.00
[Co (BTMB*) Ti Cl_2] $(NO_3)_2$	265d	Pink	38	40.34 (40.82)	2.73 (2.84)	14.70 (14.82)	7.45 (7.96)	-
[Co (BTMB*) Zr Cl_2] $(NO_3)_2$	253d	Pink	36	38.58 (38.86)	2.61 (2.73)	14.06 (14.17)	-	-
[Co (BTMB*) Sn $(CH_3)_2$] $(NO_3)_2$	238d	Pink	40	41.59 (41.92)	3.26 (3.37)	14.27 (14.39)	-	-
[Co (BTMB*) Sn $(C_2H_5)_2$] $(NO_3)_2$	227d	Pink	45	42.81 (42.99)	3.56 (3.68)	13.87 (13.98)	-	136.00
[Ni (BTMB*) Si Cl_2] $(NO_3)_2$	260d	Grey	35	41.21 (41.63)	2.79 (2.89)	15.02 (15.14)	-	-
[Ni (BTMB*) Ge Cl_2] $(NO_3)_2$	258d	Grey	36	39.33 (39.68)	2.66 (2.72)	14.34 (14.46)	-	-

Table 15 Contd.

Complex	M.P. (^{o}C)	Colour	% Yield	% Calc. (Found)				$ohm^{-1}_{cm.^{2}}$ $mol.^{-1}$
				C	H	N	Cl	
[Ni (BTMB*) Sn Cl_2] $(NO_3)_2$	260d	Grey	40	37.58 (37.83)	2.54 (2.63)	13.70 (13.88)	6.94 (7.26)	134.00
[Ni (BTMB*) Ti Cl_2] $(NO_3)_2$	263d	Grey	38	40.35 (40.47)	2.73 (2.82)	19.71 (19.88)	-	-
[Ni (BTMB*) Zr Cl_2] $(NO_3)_2$	265d	Grey	35	38.59 (38.79)	2.61 (2.72)	14.07 (14.27)	-	
[Ni (BTMB*) Sn $(CH_3)_2$] $(NO_3)_2$	220d	Grey	43	41.60 (41.98)	3.26 (3.36)	14.27 (14.38)	- -	
[Ni (BTMB*) Sn $(C_2H_5)_2$] $(NO_3)_2$	243d	Grey	45	44.05 (44.55)	3.60 (3.71)	14.27 (14.36)	-	-
[Cu (BTMB*) Si Cl_2] $(NO_3)_2$	240d	Yellow	58	41.00 (41.50)	2.77 (2.89)	14.94 (15.12)	7.58 (7.90)	136.0
[Cu (BTMB*) Ge Cl_2] $(NO_3)_2$	248d	Yellow	53	39.13 (39.68)	2.64 (2.78)	14.26 (14.39)	7.23 (7.78)	133.6
[Cu (BTMB*) Sn Cl_2] $(NO_3)_2$	253d	Yellow	55	37.40 (37.88)	2.53 (2.64)	13.63 (13.78)	6.91 (7.32)	133.2
[Cu (BTMB*) Ti Cl_2] $(NO_3)_2$	254d	Yellow	56	40.14 (40.56)	2.71 (2.84)	14.63 (14.74)	7.42 (7.96)	133.4
[Cu (BTMB*) Zr Cl_2] $(NO_3)_2$	218d	Light Brown	53	38.40 (38.83)	2.60 (2.73)	14.00 (14.13)	7.10 (7.63)	-

Table 15 Contd.

Complex	M.P. (°C)	Colour	% Yield	% Calc. (Found)				$ohm^{-1} cm.^2 mol.^{-1}$
				C	H	N	Cl	
[Cu (BTMB*) Sn $(CH_3)_2$] $(NO_3)_2$	256d	Light Brown	54	41.39 (41.84)	3.24 (2.33)	14.20 (14.36)	-	-
[Cu (BTMB*) Sn $(C_2H_5)_2$] $(NO_3)_2$	253d	Brown	54	42.62 (42.98)	3.55 (3.69)	13.81 (13.96)	-	-
[Zn (BTMB*) Si Cl_2] $(NO_3)_2$	258d	Brown	38	40.92 (41.30)	2.77 (2.88)	14.91 (14.99)	7.56 (7.92)	136.2
[Zn (BTMB*) Ge Cl_2] $(NO_3)_2$	254d	Brown	40	38.28 (38.59)	2.59 (2.73)	13.95 (13.99)	7.07 (7.48)	135.8
[Zn (BTMB*) Sn Cl_2] $(NO_3)_2$	253d	Brown	40	37.34 (37.73)	2.52 (2.68)	13.61 (13.76)	6.90 (7.30)	136.0
[Zn (BTMB*) Ti Cl_2] $(NO_3)_2$	256d	Brown	40	40.07 (40.48)	2.71 (2.82)	14.60 (14.72)	7.40 (7.82)	136.8
[Zn (BTMB*) Zr Cl_2] $(NO_3)_2$	259d	Brown	38	38.33 (38.72)	2.59 (2.68)	13.97 (14.08)	7.88 (8.30)	-
[Zn (BTMB*) Sn $(CH_3)_2$] $(NO_3)_2$	227d	Brown	42	41.32 (41.80)	3.24 (3.36)	14.17 (14.26)	-	-
[Zn (BTMB*) Sn $(C_2H_5)_2$] $(NO_3)_2$	238d	Brown	42	42.59 (42.90)	3.54 (3.68)	13.74 (13.84)	-	-
[Co(TMB*)$_2$SiCl$_2$](NO3)$_2$	263d	Pink Brown	55	44.24 (44.53)	2.99 (3.12)	16.31 (16.43)	8.18 (8.39)	

Table 15 Contd.

Complex	M.P. (°C)	Colour	% Yield	% Calc. (Found) C	H	N	Cl	$ohm_2^{-1} cm.^2 mol.^{-1}$
$[Co(TMB^*)_2GeCl_2](NO3)_2$	265	Brown	55	42.08 (42.39)	2.84 (2.96)	15.36 (15.48)	7.78 (7.79)	
$[Co(TMB^*)_2SnCl_2](NO3)_2$	268d	Brown	58	40.08 (40.38)	2.71 (2.73)	14.64 (14.76)	7.41 (7.75)	
$[Co(TMB^*)_2TiCl_2](NO3)_2$	264d	Brown	55	43.25 (43.56)	2.92 (2.99)	15.76 (15.89)	7.99 (8.23)	
$[Co(TMB^*)_2ZrCl_2](NO3)_2$	260	Brown	54	41.23 (41.63)	2.79 (2.88)	15.03 (15.23)	7.62 (7.99)	
$[Co(TMB^*)_2Sn(CH_3)_2](NO3)_2$	230d	Yellow	56	41.87 (411.90)	3.48 (3.59)	15.26 (15.38)	- -	
$[Co(TMB^*)_2Sn(C_2H_5)_2](NO3)_2$	235d	Brown	58	45.71 (45.98)	3.81 (3.94)	14.81 (14.93)	- -	
$[Ni(TMB^*)_2SiCl_2]\ (NO3)_2$	250d	Grey	53	44.25 (44.56)	2.99 (3.10)	16.13 (16.26)	8.18 (8.39)	
$[Ni(TMB^*)_2GeCl_2]\ (NO3)_2$	258d	Grey	54	42.09 (42.39)	2.84 (2.96)	15.34 (15.43)	7.78 (7.99)	
$[Ni(TMB^*)_2SnCl_2]\ (NO3)_2$	259d	Grey	55	40.09 (40.42)	2.71 (2.84)	14.13 (14.80)	7.41 (7.63)	
$[Ni(TMB^*)_2TiCl_2]\ (NO3)_2$	265d	Grey	53	43.26 (43.60)	2.92 (3.02)	15.77 (15.92)	7.99 (8.20)	

Table 15 Contd.

Complex	M.P. (°C)	Colour	% Yield	% Calc. (Found)				ohm_2^{-1} $cm.^2$ $mol.^{-1}$
				C	H	N	Cl	
$[Ni(TMB^*)_2ZrCl_2]\ (NO3)_2$	263d	Grey	54	41.24 (41.63)	2.79 (2.89)	15.03 (15.26)	7.62 (7.96)	
$[Ni(TMB^*)_2Sn(CH_3)_2](NO3)_2$	264d	Grey	54	44.50 (44.88)	3.44 (3.56)	15.27 (15.42)	- -	
$[Ni(TMB^*)_2Sn(C_2H_5)_2](NO3)_2$	263d	Grey	53	45.72 (45.89)	3.81 (3.98)	14.81 (14.99)	- -	
$[Cu(TMB^*)_2SiCl_2](NO3)_2$	256d	Yellowish green	53	44.00 (43.34)	2.97 (3.02)	16.04 (16.23)	8.13 (8.33)	
$[Cu(TMB^*)_2GeCl_2](NO3)_2$	258d	"	53	41.86 (41.89)	2.83 (2.94)	15.26 (15.38)	7.74 (7.99)	
$[Cu(TMB^*)_2SnCl_2](NO3)_2$	259	Brown	53	39.89 (39.98)	2.70 (2.86)	14.54 (14.63)	7.37 (7.68)	
$[Cu(TMB^*)_2TiCl_2](NO3)_2$	258d	Brown	53	43.02 (43.31)	2.91 (3.05)	15.68 (15.79)	7.95 (8.12)	
$[Cu(TMB^*)_2ZrCl_2](NO3)_2$	260d	Brown	55	41.03 (41.33)	2.77 (2.83)	14.96 (15.08)	7.58 (7.93)	
$[Cu(TMB^*)_2Sn(CH_3)_2](NO3)_2$	256d	Yellowish Brown	55	44.27 (44.48)	3.47 (3.59)	15.19 (15.28)	- -	
$[Cu(TMB^*)_2Sn(C_2H_5)_2](NO3)$	248d	Yellowish Brown	55	45.49 (45.78)	3.79 (3.88)	14.74 (14.93)	- -	

Table 15 Contd.

Complex	M.P. (^{o}C)	Colour	% Yield	% Calc. (Found)				$ohm_{2}^{-1} cm.^{2} mol.^{-1}$
				C	H	N	Cl	
$[Zn(TMB^{*})_2SiCl_2](NO3)_2$	240d	Brown	55	43.90 (44.26)	2.97 (2.06)	16.00 (16.20)	8.11 (8.45)	
$[Zn(TMB^{*})_2GeCl_2](NO3)_2$	243d	Brown	53	41.77 (41.99)	2.82 (2.93)	15.23 (15.34)	7.72 (7.99)	
$[Zn(TMB^{*})_2SnCl_2](NO3)_2$	245d	Brown	53	39.81 (40.13)	2.69 (2.78)	14.57 (15.68)	7.36 (7.88)	
$[Zn(TMB^{*})_2TiCl_2](NO3)_2$	245d	Brown	53	42.92 (43.16)	2.90 (2.99)	15.65 (15.19)	7.93 (8.30)	
$[Zn(TMB^{*})_2ZrCl_2](NO3)_2$	245d	Brown	53	40.94 (41.08)	2.77 (2.88)	14.92 (15.08)	7.57 (7.88)	
$[Zn(TMB^{*})_2Sn(CH_3)_2](NO3)_2$	243d	Brown	53	40.17 (44.48)	3.47 (3.58)	15.15 (15.28)	- -	
$[Zn(TMB^{*})_2Sn(C_2H_5)_2](NO3)_2$	240d	Brown	53	45.39 (45.68)	3.78 (3.89)	14.71 (14.83)	- -	

* = Deprotonated legend
d = Decompose.

Table-16: IR data of the heterobimetallic complexes of the ligands TBED, BTMB and TMB

Complex	ν NH cm^{-1}	ν C=N cm^{-1}	ν C=N cm^{-1}	ν C=C Ring Stretching Vitration cm^{-1}	ν M-N cm^{-1}	ν M-Cl cm^{-1}
[Co (TBED*) Si Cl_2] $(NO_3)_2$	3220b	1620s	1520	1450	242,425	330
[Co (TBED*) Ge Cl_2] $(NO_3)_2$	3220m	1620m	1480	1380	242,519	325
[Co (TBED*) Sn Cl_2] $(NO_3)_2$	3218m	1622m	1520	1380	242,420	330
[Co (TBED*) Ti Cl_2] $(NO_3)_2$	3220m	1618m	1480	1380	240,425	320
[Co (TBED*) Zr Cl_2] $(NO_3)_2$	3219m	1620m	1520	1380	240,425	330
[Co (TBED*) Sn $(CH_3)_2$] $(NO_3)_2$	3222m	1622m	1482	1380	240,420	-
[Co (TBED*) Sn $(C_2H_5)_2$] $(NO_3)_2$	3219m	1688m	1522	1380	240,420	-
[Ni (TBED*) Si Cl_2] $(NO_3)_2$	3222m	1620m	1482	1380	280,420	320
[Ni (TBED*) Ge Cl_2] $(NO_3)_2$	3218m	1622m	1522	1380	280,516	325
[Ni (TBED*) Sn Cl_2] $(NO_3)_2$	3222m	1620m	1480	1380	280,420	320
[Ni (TBED*) Ti Cl_2] $(NO_3)_2$	3219m	1620m	1522	1380	280,425	325
[Ni (TBED*) Zr Cl_2] $(NO_3)_2$	3220m	1620m	1480	1380	280,425	320
[Ni (TBED*) Sn $(CH_3)_2$] $(NO_3)_2$	3220m	1620m	1520	1380	280,420	-
[Ni (TBED*) Sn (C_2H_5)] $(NO_3)_2$	3220m	1622m	1480	1380	285,420	-

Table 16 contd.

Complex	ν NH cm^{-1}	ν C=N cm^{-1}	ν C=N cm^{-1}	ν C=C Ring Stretching Vitration cm^{-1}	ν M-N cm^{-1}	ν M-Cl cm^{-1}
[Cu (TBED*) Si Cl_2] $(NO_3)_2$	3220m	1618m	1520	1380	285,420	320
[Cu (TBED*) Ge Cl_2] $(NO_3)_2$	3219m	1622m	1480	1375	285,519	320
[Cu (TBED*) Sn Cl_2] $(NO_3)_2$	3219m	1620m	1545	1380	285,425	320
[Cu (TBED*) Ti Cl_2] $(NO_3)_2$	3219m	1618m	1520	1375	285,425	325
[Cu (TBED*) Zr Cl_2] $(NO_3)_2$	3219m	1622m	1480	1375	285,425	330
[Cu (TBED*) Sn $(CH_3)_2$] $(NO_3)_2$	3219m	1620m	1485	1380	285,420	-
[Cu (TBED*) Sn $(C_2H_5)_2$] $(NO_3)_2$	3250m	1640m	1485	1375	280,420	-
[Zn (TBED*) Si Cl_2] $(NO_3)_2$	3225m	1605m	1485	1376	280,420	330
[Zn (TBED*) Ge Cl_2] $(NO_3)_2$	3230m	1608m	1485	1380	280,518	330
[Zn (TBED*) Sn Cl_2] $(NO_3)_2$	3222m	1600m	1485	1380	280,425	325
[Zn (TBED*) Ti Cl_2] $(NO_3)_2$	3222m	1600m	1485	1380	280,425	325
[Zn (TBED*) Zr Cl_2] $(NO_3)_2$	3222m	1600m	1485	1380	280,425	325
[Zn (TBED*) Sn $(CH_3)_2$]$(NO_3)_2$	3222m	1600m	1485	1380	280,425	-
[Zn (TBED*) Sn$(C_2H_5)_2$] $(NO_3)_2$	3222m	1600m	1485	1380	280,425	-

Table 16 contd.

Complex	ν_{NH} cm^{-1}	$\nu_{C=N}$ cm^{-1}	$\nu_{C=N}$ cm^{-1}	ν_{C-S} cm^{-1}	ν_{M-N} cm^{-1}	ν_{M-Cl} cm^{-1}
$[Co(BTMB^*)_2 Si Cl_2](NO_3)_2$	3226m	1624s	1520	730	242,425	330
$[Co(BTMB^*)_2 Ge Cl_2](NO_3)_2$	3226m	1624m	1480	730	242,519	325
$[Co(BTMB^*)_2 Sn Cl_2](NO_3)_2$	3218m	1622m	1520	730	242,420	330
$[Co(BTMB^*)_2 Ti Cl_2](NO_3)_2$	3220m	1618m	1480	730	280,425	320
$[Co(BTMB^*)_2 Zr Cl_2](NO_3)_2$	3218m	1620m	1520	732	240,425	330
$[Co(BTMB^*)_2 Sn(CH_3)_2](NO_3)_2$	3220m	1622m	1482	733	240,420	-
$[Co(BTMB^*)_2 Sn(C_2H_5)_2](NO_3)_2$	3218m	1688m	1522	730	240,420	-
$[Ni(BTMB^*)_2 Si Cl_2](NO_3)_2$	3220m	1620m	1482	730	280,420	320
$[Ni(BTMB^*)_2 Ge Cl_2](NO_3)_2$	3222m	1622m	1522	734	280,516	325
$[Ni(BTMB^*)_2 Sn Cl_2](NO_3)_2$	3222m	1620m	1480	730	280,420	320
$[Ni(BTMB^*)_2 Ti Cl_2](NO_3)_2$	3219m	1620m	1522	730	280,425	325
$[Ni(BTMB^*)_2 Zr Cl_2](NO_3)_2$	3219m	1620m	1480	736	280,425	320
$[Ni(BTMB^*)_2 Sn(CH_3)_2](NO_3)_2$	3220m	1620m	1520	733	280,420	-
$[Ni(BTMB^*)_2 Sn(C_2H_5)](NO_3)_2$	3220m	1622m	1480	734	285,420	

Table 16 contd.

Complex	ν NH cm^{-1}	ν C=N cm^{-1}	ν C=N cm^{-1}	ν C-S cm^{-1}	ν M-N cm^{-1}	ν M-Cl cm^{-1}
$[Cu(BTMB^*)_2 Si Cl_2](NO_3)_2$	3220m	1618m	1520	735	285,420	320
$[Cu(BTMB^*)_2 Ge Cl_2](NO_3)_2$	3219m	1622m	1480	733	285,519	320
$[Cu(BTMB^*)_2 Sn Cl_2](NO_3)_2$	3219m	1620m	1545	730	285,425	320
$[Cu(BTMB^*)_2 Ti Cl_2](NO_3)_2$	3219m	1618m	1520	720	285,425	325
$[Cu(BTMB^*)_2 Zr Cl_2](NO_3)_2$	3219m	1622m	1480	736	285,425	330
$[Cu(BTMB^*)_2 Sn(CH_3)_2](NO_3)_2$	3219m	1620m	1485	730	285,420	
$[Cu(BTMB^*)_2 Sn(C_2H_5)_2](NO_3)_2$	3250m	1640m	1485	734	280,420	
$[Zn(BTMB^*)_2 Si Cl_2](NO_3)_2$	3225m	1605m	1485	736	280,420	330
$[Zn(BTMB^*)_2 Ge Cl_2](NO_3)_2$	3230m	1608m	1485	730	280,518	330
$[Zn(BTMB^*)_2 Sn Cl_2](NO_3)_2$	3222m	1600m	1485	732	280,425	325
$[Zn(BTMB^*)_2 Ti Cl_2](NO_3)_2$	3222m	1600m	1485	736	280,425	325
$[Zn(BTMB^*)_2 Zr Cl_2](NO_3)_2$	3222m	1600m	1485	732	280,425	325
$[Zn(BTMB^*)_2 Sn(CH_3)_2](NO_3)_2$	3222m	1600m	1485	737	280,425	-
$[Zn(BTMB^*)_2 Sn(C_2H_5)_2](NO_3)_2$	3222m	1600m	1485	730	280,425	-

Table 16 contd.

Complex	ν_{NH} cm^{-1}	$\nu_{C=N}$ cm^{-1}	$\nu_{C=N}$ cm^{-1}	ν_{C-S} cm^{-1}	ν_{M-N} cm^{-1}	ν_{M-Cl} cm^{-1}
[Co $(TMB^*)_2$ Si Cl_2] $(NO_3)_2$	3220b	1620s	1520	730	242,425	330
[Co $(TMB^*)_2$ Ge Cl_2] $(NO_3)_2$	3220m	1620m	1480	734	242,519	325
[Co $(TMB^*)_2$ Sn Cl_2] $(NO_3)_2$	3218m	1622m	1520	735	242,420	330
[Co $(TMB^*)_2$ Ti Cl_2] $(NO_3)_2$	3220m	1618m	1480	732	240,425	320
[Co $(TMB^*)_2$ Zr Cl_2] $(NO_3)_2$	3219m	1620m	1520	730	240,425	330
[Co $(TMB^*)_2$ Sn $(CH_3)_2$] $(NO_3)_2$	3222m	1622m	1482	733	240,420	
[Co $(TMB^*)_2$ Sn $(C_2H_5)_2$] $(NO_3)_2$	3219m	1688m	1522	734	240,420	
[Ni $(TMB^*)_2$ Si Cl_2] $(NO_3)_2$	3222m	1620m	1482	730	280,420	320
[Ni $(TMB^*)_2$ Ge Cl_2] $(NO_3)_2$	3218m	1622m	1522	732	280,516	325
[Ni $(TMB^*)_2$ Sn Cl_2] $(NO_3)_2$	3222m	1620m	1480	736	280,420	320
[Ni $(TMB^*)_2$ Ti Cl_2] $(NO_3)_2$	3219m	1620m	1522	737	280,425	325
[Ni $(TMB^*)_2$ Zr Cl_2] $(NO_3)_2$	3220m	1620m	1480	732	280,425	320
[Ni $(TMB^*)_2$ Sn $(CH_3)_2$] $(NO_3)_2$	3220m	1620m	1520	734	280,420	
[Ni $(TMB^*)_2$ Sn (C_2H_5)] $(NO_3)_2$	3220m	1622m	1480	737	285,420	

Table 16 contd.

Complex	ν NH cm^{-1}	ν C=N cm^{-1}	ν C=N cm^{-1}	ν C-S cm^{-1}	ν M-N cm^{-1}	ν M-Cl cm^{-1}
$[Cu\ (TMB^*)_2\ Si\ Cl_2]\ (NO_3)_2$	3229m	1618m	1520	735	285,420	320
$[Cu\ (TMB^*)_2\ Ge\ Cl_2]\ (NO_3)_2$	3230m	1622m	1480	732	285,519	320
$[Cu\ (TMB^*)_2\ Sn\ Cl_2]\ (NO_3)_2$	3216m	1620m	1545	734	285,425	320
$[Cu\ (TMB^*)_2\ Ti\ Cl_2]\ (NO_3)_2$	3219m	1618m	1520	737	285,425	325
$[Cu\ (TMB^*)_2\ Zr\ Cl_2]\ (NO_3)_2$	3219m	1622m	1480	732	285,425	330
$[Cu\ (TMB^*)_2\ Sn\ (CH_3)_2]\ (NO_3)_2$	3226m	1620m	1485	736	285,420	
$[Cu\ (TMB^*)_2\ Sn\ (C_2H_5)_2]\ (NO_3)_2$	3230m	1640m	1485	737	280,420	
$[Zn\ (TMB^*)_2\ Si\ Cl_2]\ (NO_3)_2$	3225m	1605m	1485	732	280,420	330
$[Zn\ (TMB^*)_2\ Ge\ Cl_2]\ (NO_3)_2$	3230m	1608m	1485	736	280,518	330
$[Zn\ (TMB^*)_2\ Sn\ Cl_2]\ (NO_3)_2$	3222m	1600m	1485	733	280,425	325
$[Zn\ (TMB^*)_2\ Ti\ Cl_2]\ (NO_3)_2$	3222m	1600m	1485	734	280,425	325
$[Zn\ (TMB^*)_2\ Zr\ Cl_2]\ (NO_3)_2$	3222m	1600m	1485	737	280,425	325
$[Zn\ (TMB^*)_2\ Sn\ (CH_3)_2](NO_3)_2$	3222m	1600m	1485	736	280,425	-
$[Zn\ (TMB^*)_2\ Sn(C_2H_5)_2]\ (NO_3)_2$	3222m	1600m	1485	730	280,425	-

Table 17: Magnetic moment and electronic spectral data of the representative heterobimetallic complexes of (BTMB)

Complex	u eff (B.M.)	Electronic spectra	Assignment
$[Co(BTMB^*)SnCl_2](NO_3)_2$	4.83	41,666 cm^{-1}	Charge transfer
		37,735 cm^{-1}	
		18,518 cm^{-1}	$^4T_{1g}$ (P) <----- $^4T_{1g}$ (F)
		13,888 cm^{-1}	$^4A_{2g}$ (P) <----- $^4T_{1g}$ (F)
$[Ni(BTMB^*)SnCl_2](NO_3)_2$	3.41	37,313 cm^{-1}	Charge transfer
		25,641 cm^{-1}	$^3T_{1g}$ (P) <------ $^3A_{2g}$ (F)
		13,888 cm^{-1}	$^4T_{1g}$ (F) <------ $^3A_{2g}$ (F)
$[Cu(BTMB^*)SnCl_2](NO_3)_2$	1.78	39,215 cm^{-1}	Charge transfer
		37,037 cm^{-1}	$^2T_{2g}$ <------ ^2Eg
		31,250 cm^{-1}	
		33,222 cm^{-1}	
		12,406 cm^{-1}	

Table 18: % Inhibition data, ((a) A. flavus (b) A. niger (c) A. pori), % mortality and LD_{50} of cockroaches of metal complexes of TBED, TMB, BTM and their heterobimetallic complexes

Complex	Concentration	% Inhibition		
		(a)	(b)	(c)
Cu (TBED) $(NO3)_2$	2.00	60	58	55
	2.50	62	60	59
	3.00	63	61	61
[Cu $(TBED^*)SnCl_2](NO3)_2$	2.00	63	62	60
	2.50	65	63	61
	3.00	65	64	63
[Cu $(TMB)_2(NO3)_2$	2.00	65	66	66
	2.50	68	67	68
	3.00	70	70	70
[Cu$(TMB^*)_2SnCl_2](NO3)_2$	2.00	68	67	67
	2.50	70	70	70
	3.00	74	73	73
[Cu $(BTMB^*)$ $SnCl_2]$ $(NO3)_2$	2.00	73	68	69
	2.50	75	73	74
	3.00	78	75	76

Table 18 contd.

% Mortality and LD_{50} values

Complex	Log concentration in ppm x 100	% Mortality	Probit value	LD_{50}
$[Cu(TBED)](NO3)_2$	2.69	10	3.7184	
	2.77	20	4.1584	
	2.84	30	4.4756	8.91
	2.90	40	4.7467	
	2.95	50	5.0000	
$[Cu(TBED^*)SnCl_2](NO_3)_2$	2.00	20	4.1584	
	2.30	30	4.4756	
	2.47	40	4.7467	7.94
	2.60	50	5.0000	
	2.69	60	5.2533	
$[Cu(TMB)_2](NO3)_2$	2.00	20	4.1584	
	2.30	33	4.5684	
	2.47	50	5.0000	6.91
	2.60	70	5.5244	
	2.69	80	5.8416	
$[Cu(TMB^*)SnCl_2](NO3)_2$	2.00	33	4.5684	
	2.30	40	4.7467	
	2.47	60	5.2533	6.31
	2.60	70	5.5244	
	2.69	80	5.8416	
$[Cu(TMB)SnCl_2](NO3)_2$	2.00	40	4.7467	
	2.30	60	5.2533	
	2.47	70	5.5244	5.37
	2.60	80	5.8416	
	2.69	100	--	

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